A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION OF COPOLYMERS OF VINYL ALCOHOL

BY

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To my mother and father.

PREFACE

The work described in this thesis was carried out by the author during the period October, 1973 to September, 1976 at the University of Glasgow, in the Department of Physical Chemistry, which is under the supervision of Professor G.A. Sim.

I should like to thank my supervisor Professor N. Grassie for suggesting the topic of this thesis and for his interest, advice and constant encouragement throughout the course of the work.

My thanks are due to my colleagues in the Macromolecular Chemistry groups for helpful discussion and suggestions, and to various members of the technical staff of the Chemistry Department.

Finally, I should like to thank Mrs. J. Mackinnon for typing the manuscript.

M. FEROZE BAKHAT.

SUMMARY

Since poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl butyral) and their intermediate copolymers are important commercial plastics and since it is important that commercial materials should be as stable as possible to the environment, a great deal of attention has been given studying the relationship between the synthesis and thermal stability of these materials.

Brief notes on the general concept of polymer degradation, the history of poly(vinyl acetate), poly(vinyl alcohol) and poly(vinyl butyral) and their commercial importance in various fields are given in Chapter 1. The introductory chapter also reviews briefly the relationships between the chemical structure and thermal stability of vinyl copolymers.

Chapter 2 includes a list of material used in this work and gives a description of the apparatus and experimental techniques employed in the present study. The first part deals with the method of preparation of the copolymers of vinyl alcohol and the second section describes the techniques of thermal analysis used to identify the degradation products.

A detailed study of the hydrolysis of poly(vinyl acetate) is given in Chapter 3. The initial rate is independent of the NaOH/ester ratio and reaction follows second order kinetics in the initial stages. The rate of a reaction responds to solvent composition, reaction temperature and the nature of the catalyst. In the ethanol/H_2O solvent system, the rate is enhanced by a closer coiling of the macromolecules.

The thermal degradation of poly(vinyl acetate) and copolymers of vinyl acetate and vinyl alcohol is discussed in detail in Chapter 4.

The copolymers are less stable than poly(vinyl acetate) below 340°C but exhibit greater stability at higher temperature. There is no interaction between vinyl alcohol units during thermal degradation of the copolymer.

In Chapter 5 the thermal degradation properties of poly(vinyl alcohol) and copolymers of vinyl alcohol and vinyl butyral are described. Poly(vinyl alcohol) loses water in a chain reaction similar to that in which poly(vinyl acetate) eliminates acetic acid. There is no interaction between vinyl alcohol and vinyl butyral units during degradation of vinyl alcohol/vinyl butyral copolymer. The main degradation products are butyraldehyde and water. The thermal stability to weight loss may depend upon the extent of Stevic interaction between vinyl butyral units in the chain. Greater interaction between them results less stable copolymers.

CONTENTS

CHAPTER ONE

INTRODUCTION

1. Polymer Degradation (General).

A. Introduction. Polymers in everyday use are subjected to a variety of modifying influences, one or more of which may be in operation at any given time, depending on the particular environment and application of the material. These influences include the action of heat, light (or higher energy radiation), mechanical stresses, the atmosphere, chemicals and bacteria.

In classical chemical usage, the term "degradation" implies a breaking down of chemical structure and in polymer chemistry this would be equivalent to a fall in molecular weight. However, polymer degradation is now generally regarded as any deterioration of those properties which make the material commercially useful as a plastic, rubber or fibre. A decrease in molecular weight is not always involved.

Quite often, the loss of one useful property may lead to the development of another, so that degradation can be used to extend the application of the polymer. Because of this, the term "degradation" will be used in its broadest sense to cover all chemical reactions of polymers.

A useful approach to the understanding of polymer degradation is to study each modifying agency separately and then try to deduce their combined effect. Clearly this approach has many short-comings and is only adopted for ease of study.

This work deals with the thermal degradation of vinyl-type polymers of general structure $\leftarrow CH_2 - CXY \rightarrow_n$, where X is hydrogen and Y a functional group.

B. The Reasons For Studying Thermal Degradation. Studies of the thermal degradation behaviour of polymers are of prime importance from a scientific point of view, as they may help to reveal details of molecular structure, such as the sequence and arrangements of the repeating units or monomers, and side groups in the polymer or co-polymer chain, as well as the nature of the chain ends.

Similar thermal degradation studies of polymers are of extreme importance from a practical point of view. They may not only explain the behaviour of polymers under conditions of high temperatures but also help in selecting the right kind of already existing material for specific uses where high temperatures are encountered, and what is sometimes more important, suggest the design and synthesis of new materials to meet new or existing requirements.

C. The Mechanism of Thermal Degradation (General). The thermal degradation mechanisms of polymers fall into two distinct categories.

(a) Chain-Scission reactions.

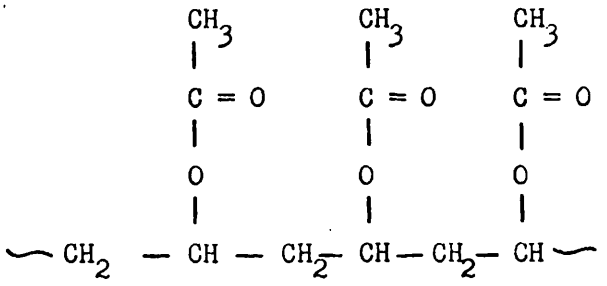
(b) Substituent reactions.

Chain-scission reactions involve rupture of the main backbone of the polymer molecule. The products at any intermediate stage of the reaction are similar to the parent material in the sense that the monomer units are still distinguishable in the chains. New types of end-groups may or may not appear, depending upon the nature of the chain-scission process.

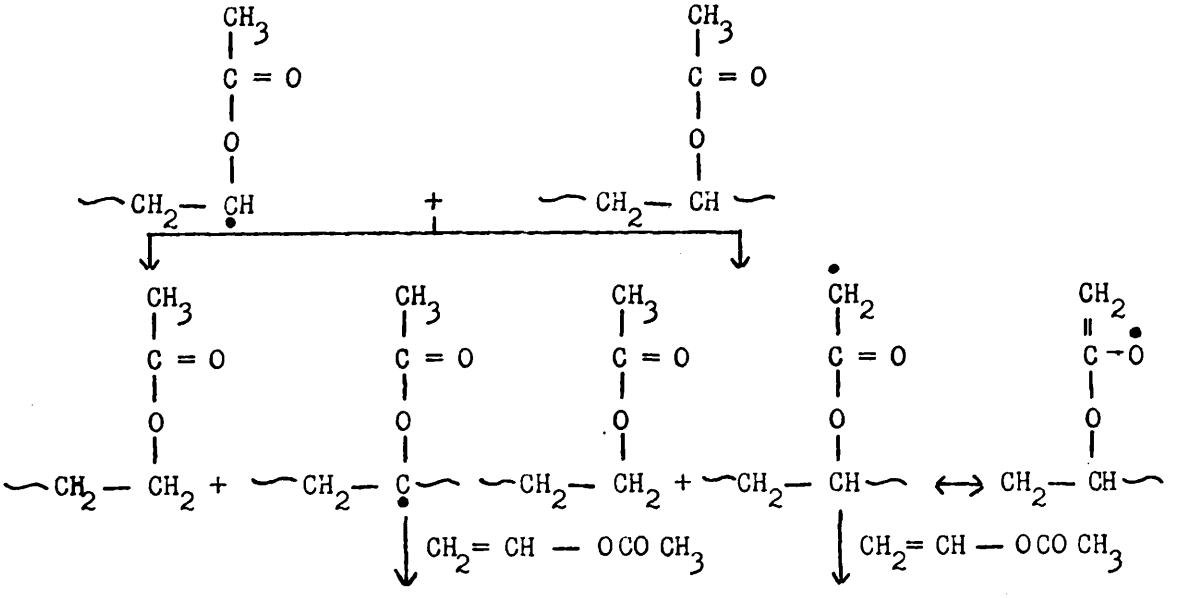
Substituent reactions involve modification or total elimination of the substituents attached to the polymer backbone. The latter is not broken, but the chemical nature of the repeating unit in the macromolecule is changed. Any volatile products are chemically unlike monomer.

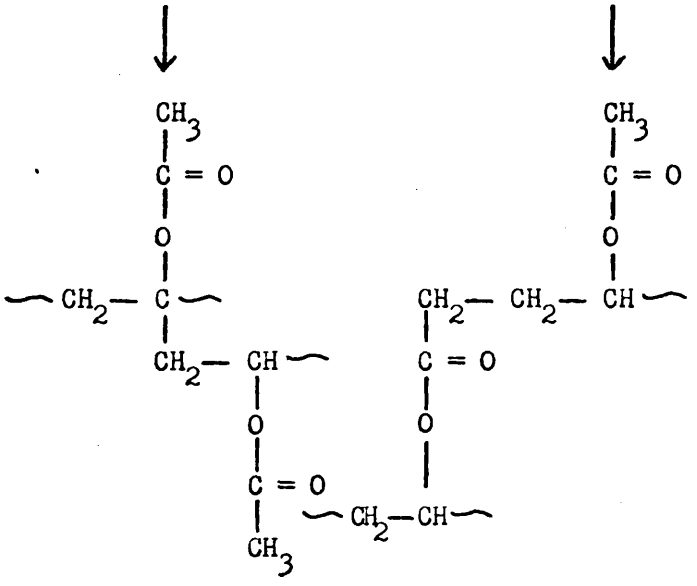
2. Preparation and Structure of Polymers.

A. Poly(vinyl acetate), (PV-OAc). PV-OAc is one of the most important commercial poly(vinyl esters). It is utilised not only as a plastic, primarily in the form of emulsion, but also as an intermediate for the manufacture of a poly(vinyl alcohol), (PV-OH), poly(vinyl butyral), (PVB), and other similar materials which cannot be prepared by direct polymerisation of the monomer. PV-OAc is normally prepared by the use of free radical initiators in bulk, solution or emulsion. It has been shown [1] that PV-OAc has a predominantly head-to-tail structure and becomes increasingly branched as the degree of conversion



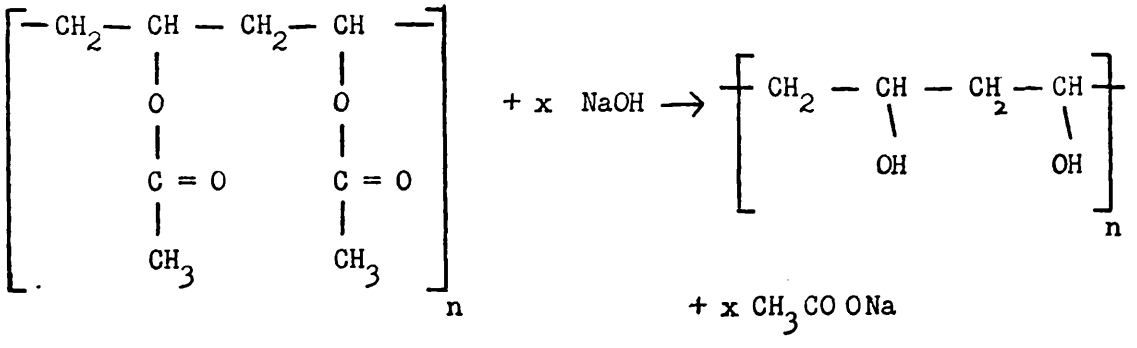
is increased. Branching occurs because of chain transfer. Since a growing radical may abstract a hydrogen atom from either the chain or the methyl group, two kinds of branches are possible:



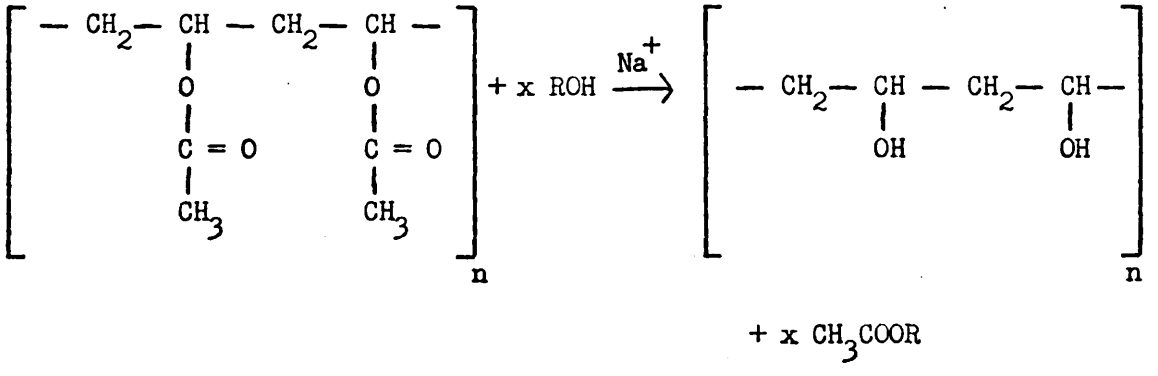


The radical resulting from transfer to methyl group is stabilised by delocalisation and in practice, most branching occurs at the side groups; branching from chain methylene groups occurs only to a small extent.

B. Poly(vinyl alcohol), (PV-OH). Since the monomer does not exist, the starting material for the production of PV-OH is polymerised ester, usually PV-OAc. PV-OH was first prepared in 1924 by Herrmann and Haehnel [2,3] by saponification.



In 1932 Herrman, Haehnel and Berg [4] reported the more elegant ester interchange reaction method.

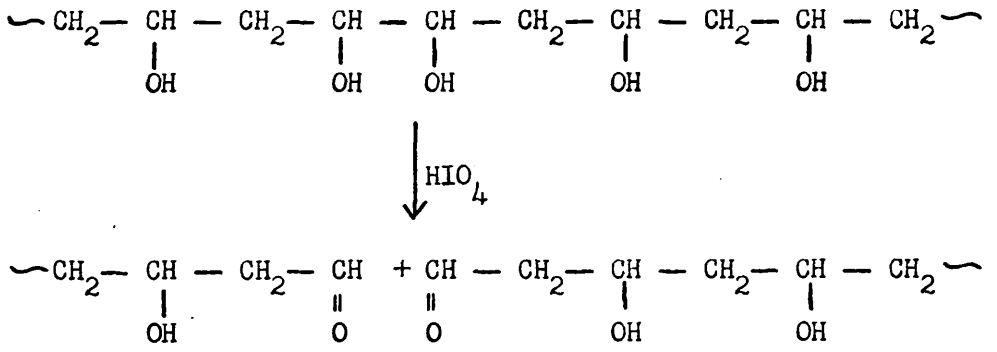


where R = CH_3, C_2H_5, C_3H_7, C_4H_9.

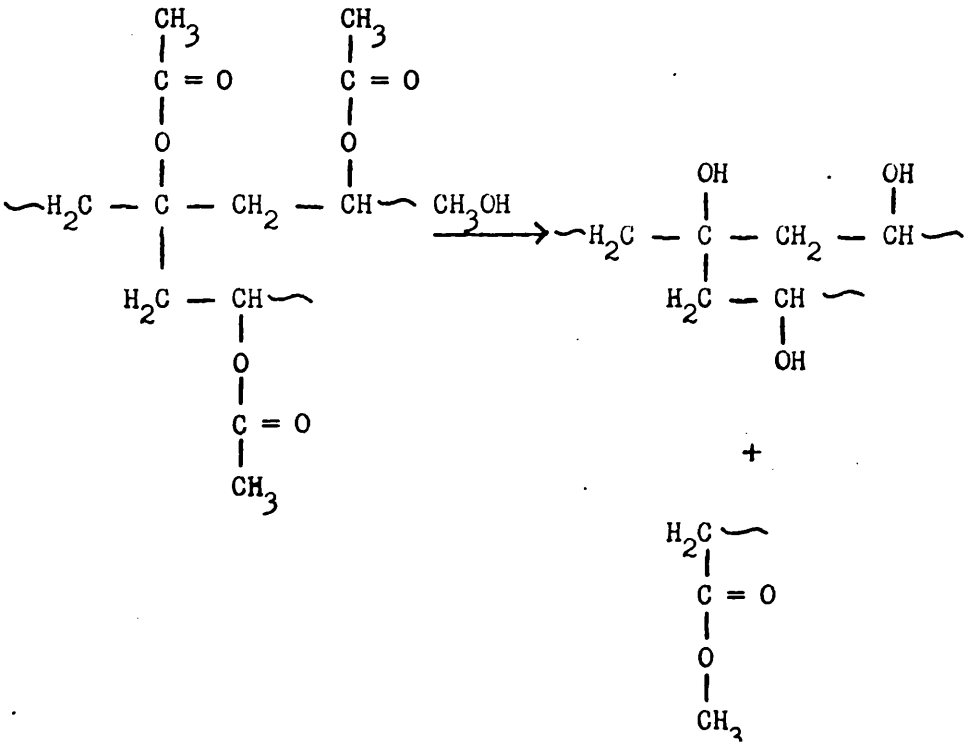
By means of ester interchange, acetic ester is obtained. Since these esters are volatile solvents, it is possible to remove from the PV-OH by simple distillation.

Most of the work on the topic up to the beginning of the 1940's is described by Kainer [5]. The bulk of the work, however, has appeared more recently, during the 1950's, when PV-OH was used as the basis of a textile-fibre industry. This possibility had indeed been suggested by Herrmann and Haehnel in 1931 [6], but the break-through came later with the work of Sakurada, Yazawa and Tomanari [7], who first used the acetalised fibre in 1938. In an improved form in 1948, this created the basis for the large industrial enterprise devoted to fibre production in Japan. The acetalised fibre, which has a certain resemblance to cotton and viscose rayon, has not, however, achieved world wide importance. Its importance could, however, increase quickly, since, with the rapid increase in the world's population, it will become necessary to employ more and more of the Earth's surface for food production, and the cultivation of cotton will thereby be reduced. Hackel has reviewed technical production methods generally [8].

(a) Structure. PV-OH has a predominantly head-to-tail structure since it is derived from PV-OAc. It has a few head-to-head linkages (1-2% of the total linkages). This feature was originally detected by periodic acid degradation at the 1, 2-glycol bond followed by viscometric study of the resulting cleaved polymer [10, 11] and was confirmed by measurement of the acid consumed by titration [12, 13] and by polarographic methods [14].



As mentioned previously (section 2, A), two types of branching may occur in PV-OAc. The alcoholysis of PV-OAc causes removal of branches resulting from chain transfer to the acetate group but not those arising from transfer to chain hydrogen:



There appears to be little branching in PV-OH, from which it may be deduced, since most of the branching in PV-OAc arises from transfer to the acetate group. Since PV-OAc, as normally prepared, is atactic, PV-OH is also atactic. However, although PV-OAc is amorphous, PV-OH exhibits crystallinity.

C. Vinyl Acetate/Vinyl Alcohol Copolymers, (V-OAc/V-OH).

Copolymers of V-OAc and V-OH have been prepared by various workers in three ways, by saponification of PV-OAc, by alcoholysis of PV-OAc, and by reacetylation of PV-OH. In this present work copolymers have been prepared by all three methods (see Chapter Two).

The structure of the copolymers depends upon the method used. Reacetylation of PV-OH gives rise to random copolymers [15, 16, 17], while the other two methods give rise to block copolymers.

D. Vinyl Alcohol/Vinyl Butyral Copolymers, (V-OH/VB). When the hydroxyl groups in PV-OH are condensed with an aldehyde, poly(vinyl formal), poly(vinyl acetal), poly(vinyl butyral) etc. are formed depending upon the specific aldehyde used.

At Shawinigan Falls, Quebec, PV-OAc was condensed directly with aldehyde in the presence of acidic catalysts [18]. The partially converted PV-OHs obtained were tougher and harder than the PV-OAc starting materials. Others also prepared the copolymers by direct reaction of PV-OAc with aldehydes using mineral acid catalysts [19]. In Germany PV-OH in solution was reacted with aldehyde in the presence of mineral acids before 1930 [20]. An early condensation was carried out in a mixture of alcohol and methylene chloride with a small amount of sulphuric acid as catalyst. Large scale development of aldehyde modified PV-OH took place in America, with poly(vinyl formal) (PVF), for wire covering (Shawinigan) and PVB for auto-safety glass

inter-layer (du Pont, Monsanto and Carbide). In one method PV-OH obtained by sulphuric acid alcoholysis was used directly without drying or neutralisation [21]. In France quite different methods had been developed for the preparation of these materials. In one Nobel process PV-OAc was first hydrolysed by hydrochloric acid in a mixer at room temperatures in the presence of water and alcohol [22]. The aldehyde was then added directly, and condensation was carried out at moderate temperatures. In a plant method [23], the hydrolysis of PV-OAc and reaction with aldehyde occurred simultaneously in a mixed solvent containing butanol and butyl acetate, and in the presence of an acid catalyst. Detailed information on the production of PVB is also available in the Soviet literature [24].

3. Uses of Poly(vinyl acetate), Poly(vinyl alcohol) and Poly(vinyl butyral).

A. Poly(vinyl acetate). The most important uses of PV-OAc are as follows:-

(i) In the production of water based emulsion paints.

(ii) For the production of adhesives, both of the emulsion type and of the hot-melt type.

(iii) As a starting material for the production of PV-OH.

It is common practice to plasticise PV-OAc intended for surface coatings by such materials as dibutyl phthalate. A limitation of external plasticisers of this kind is that they may eventually be lost by evaporation or by migration into the substrate, leaving an imperfect and brittle film. This limitation may be overcome by the use of co-polymers and these are now widely used in surface coatings and other applications.

B. Poly(vinyl alcohol). The most important uses of PV-OH are as follows:-

(i) In the textile industry it is used as a warp size, as a finishing resin to impart stiffness to a fabric, and as a binder for non-woven fabrics.

(ii) In the paper industry it is used as a binder in size press coatings, while PV-OH fibres have been added to pulp to improve the internal properties of paper.

(iii) PV-OH solutions in water are excellent adhesives for gluing paper to paper and paper to wood. PV-OH has replaced starches and dextrins to a certain extent in the manufacture of gummed labels and envelopes. PV-OH together with PV-OAc constitutes the so called "white glue" usually used for gluing wood in the furniture industry.

(iv) It has been proposed for coatings for all kinds of substrates.

C. Poly(vinyl butyral). The most important uses of PVB are as follows:-

(i) PVB is an important ingredient of so called "wash-primer." Wash-primers are widely used on a variety of metal structures such as storage tanks, ships, aeroplanes etc.

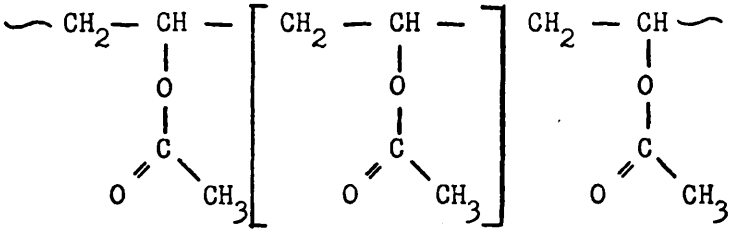
(ii) It is used fairly widely as a sealer in wood finishes where it confers outstanding "hold out" inter-coat adhesion, moisture resistance, flexibility, toughness and impact resistance. It has also been proposed for heat-sealable coatings, temperature coatings for packaging applications and can coatings.

(iii) The largest use of PVB is as the plastic inter-layer for auto-motive and air-craft safety glazing. Advantages of the

resin as an inter-layer are its superior adhesion to glass, toughness, stability on exposure to sunlight, clarity and insensitivity to moisture.

4. Previous Work on the Thermal Degradation of the Polymers.

A. Poly(vinyl acetate). The earliest report on the products of the thermal degradation of PV-OAc was by Noma [25] in 1948. He obtained 72% of the theoretical amount of acetic acid by dry distilling the polymer at 250-300°C. It was concluded that the initial scission occurred at the polymer side chains (ie., the acetate group). Sobue and co-workers [26] reported in 1949 that PV-OAc decreases in molecular



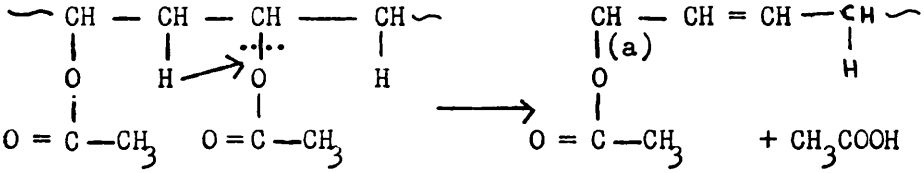
weight on heating at temperatures between 280°C and 300°C.

The first detailed study on the subject of the thermal degradation of PV-OAc was reported by Grassie [27]. The volatile degradation products of PV-OAc in vacuo (up to 260°C) were acetic acid with smaller amounts of water, and carbon dioxide and a trace of ketene. The water, carbon dioxide and ketene were consistent with the decomposition of the acetic acid.

The colour of the residual polymer was attributed to conjugated structures and it was concluded that the residue was polyenic and could be described as polyacetylene. The detection of benzene (spectroscopically) among the products in the later stages of the reaction (at higher temperatures) supported this proposal.

Based upon the rate of evolution of acetic acid, a non radical

chain mechanism was proposed. The conjugated structure of the polymeric residue also favours a chain reaction passing from unit to unit rather than random removal of acetic acid. Madorsky [28] has suggested that initiation of deacetylation can be explained by thermal scission of C-O bonds, occurring randomly along the chain, C-O bonds being weaker than C-C bonds. He further suggests that this is followed by abstraction of a hydrogen atom from an adjacent carbon atom to form acetic acid and a double bond in the chain. Since the C-O bond (a)



is now in the β-position to a double bond in the polymer molecule, it breaks more easily than the other C-O bonds in the chain and formation of acetic acid thus proceeds as a chain reaction. In some cases, abstraction of a hydrogen atom by an acetate free radical may take place intermolecularly, thus resulting in cross-linkages.

Paulinec and Kaloforov [29] consider the observed rapid cross-linking of PV-OAc surprising, if initiation of deacetylation at chain ends only, be assumed. These workers have postulated that all the acetate groups have the same reactivity, leading to random loss of acetic acid along the polymer chain. The existence of a conjugated polymer residue has been confirmed by ultra-violet spectroscopy studies of the degraded polymer residue. Gardner and McNeill [30] found six or more double bonds in conjugation, less than degraded PVC, while Zimmermann [31] detected polyenes with up to twelve conjugated double bonds in discoloured PV-OAc.

Grassie [27] found that, while acetic acid accounted for up to 95% of the evolved volatiles, about 5% consisted of carbon dioxide, water and ketene, all of which, it was suggested, arise from acetic acid decomposition. Serrotte and Desreux [32] did not observe

carbon dioxide and ketene but Gardner and McNeill [30] using TVA and I.R. spectroscopy have observed carbon dioxide, ketene, carbon monoxide and methane (besides acetic acid), although no deductions were made about possible mechanisms of formation. Although the overall reaction has been clearly formulated, the detailed mechanism of PV-OAc degradation has not been fully elucidated.

B. Poly(vinyl alcohol). The thermal stability of PV-OH has been investigated by numerous workers over the past two decades [25, 33-43]. In general, PV-OH, when pyrolysed, undergoes dehydration and depolymerisation. Decomposition of PV-OH proceeds in two stages. The first stage mainly involves dehydration accompanied by the formation of some volatile products. The residues are predominantly polymers with conjugated unsaturated structures. In the second stage, the polyene residues are further degraded at 450°C to yield carbon and hydrocarbons [43]. The product distribution in the two stages of decomposition is presented in Table 1.1.

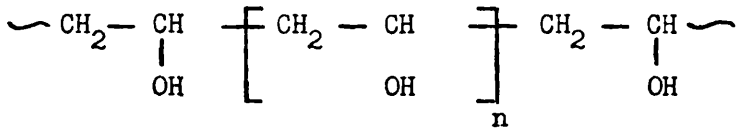
Table 1.1.

Decomposition products of PV-OH (material balance, in percentage by weight of original polymer)*

First stage (240°C, 4h)				Second stage (450°C, 4h)		
Volatiles 47·9	Water layer	Water	33·4	Volatiles 27·7	Water layer	0·60
		Organic compounds	1·56			
	Oil layer	Organic compounds analysed	1·19		Oil layer	22·30
		Not analysed	4·99			
	Gas 0·92				Gas 2·46	
	Loss 5·81				Loss 2·34	
Residue 52·1				Residue 24·4		

*Taken from Y. Tsuchiya and K. Sumi, J.Polym.Sci., A-1, 7, 3151 (1969).

Noma [25], in 1948, collected the volatiles from the thermal degradation of PV-OH. Water, crotonaldehyde and acetaldehyde were found among the volatile products. In a later study [44] it was



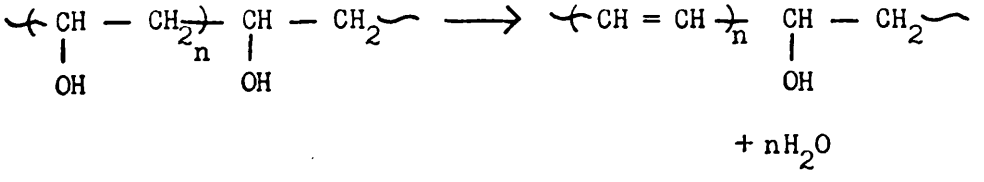
concluded that this initial work described oxidative degradation, since the products were not detected when the reaction was carried out in an atmosphere of carbon dioxide. Ukida and co-workers [33] observed that there were no apparent changes in the number of residual double bonds and carbonyl groups or in the colour of the residual polymer on heating PV-OH in nitrogen at 195°C. However, in air, the number of double bonds and carbonyl groups increased and the residue became insoluble in hot water. Futama and Tanaka [35] used mass spectrometry to identify the products of thermal treatment of PV-OH films. Water and acetaldehyde were found as the major volatile products. The major product, water, was formed principally in two stages, namely, at 90°C and 200°C. The water liberated at the latter temperature was thought to be the result of a dehydration reaction on the polymer chain, whereas the former was considered water trapped in the polymer matrix.

Other investigators [36] have used I.R. analysis to identify the degradation products. Very few changes in either the infra-red spectrum or the elemental analysis of the polymer were found when samples were heated at lower temperatures in vacuo. However, on heating in air, film samples became coloured, and the I.R. spectrum exhibited changes interpreted as an increase in carbonyl content (i.e., increased carbonyl absorption). On degradation of the film at higher temperatures in vacuo, in nitrogen and in air, the following products were isolated and identified in addition to water: acetaldehyde,

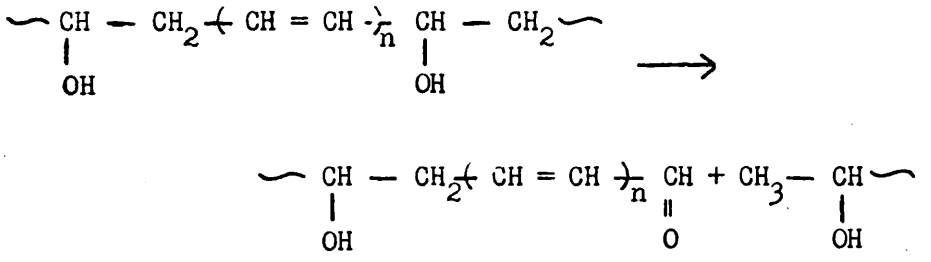
crotonaldehyde, benzaldehyde and phenyl acetate. The quantities found were not reported. The I.R. spectrum of the pyrolysis residues indicated a greater carbonyl content than was present in the original polymer. In the later report, the same investigators [37] interpreting the results, suggested that the colouration of the polymer resulted from the formation of carbonyl species and that the aldehydes formed are the result of secondary complex degradation reactions of the autoxidised polymer.

Ettre and Varadi [39], using gas chromatographic techniques, examined the pyrolysis products of PV-OH. They found that acetaldehyde, acetic acid, and water were the major products at temperatures ranging from 500°C to 600°C. At 700°C amounts of carbon monoxide and carbon dioxide significantly increased. Above that temperature, the major products become carbon dioxide, carbon monoxide and methane. There were some unidentified products at lower temperatures which may well be the aldehydes reported in earlier investigations. Further I.R. spectral studies by Gel'fman and co-workers [45] reported an increase in the concentration of isolated and conjugated carbon-carbon double bonds, as the temperature of pyrolysis was increased (from 250°C to 350°C). These results were found whether pyrolysis was carried out in air or in an inert atmosphere such as nitrogen.

Gilbert and Kipling [40] have suggested that the mechanism of the thermal degradation of PV-OH under vacuum might be similar to that of PV-OAc. Tsuchiya and Sumi [43] have deduced the similar degradation mechanism for PV-OH. At 245°C water is split off the polymer chain, and a residue with a conjugated polyene structure results:



Scission of several carbon-carbon bonds leads to the formation of carbonyl ends. For example, aldehyde ends probably arise from the reaction:



A similar mechanism yields methyl ketone ends by degradation of the polymers containing ketone carbonyl groups [35,36].

In the second stage pyrolysis of PV-OH, the volatile products consist mainly of aromatic hydrocarbons. Since the qualitative and quantitative composition of the degradation products of PV-OH are very similar to those of PV-OAc and PVC, it can be concluded that the same mechanism applied to the second-stage decomposition of all three types of vinyl polymers.

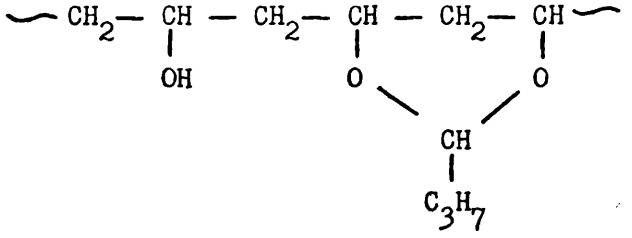
Futama and Tanaka [35] have also reported the formation of volatile vapours, water and acetaldehyde from PV-OH pyrolysed at 185-350°C. Similar observations were made by D.L. Gardner and I.C. McNeill [30]. They used Thermal Volatilisation Analysis (TVA) and Ultra-violet Spectroscopy techniques to investigate the thermal elimination reactions of the polymer.

C. Vinyl Acetate/Vinyl Alcohol Copolymers. Nothing has been published in literature about the thermal degradation mechanism of V-OAc/V-OH copolymers. However some investigations have been made on some related copolymer systems which will be discussed in brief in Chapter Four.

Robert K. Tubbs [17] studied copolymers of V-OAc/V-OH by differential thermal analysis (DTA), but his investigations were

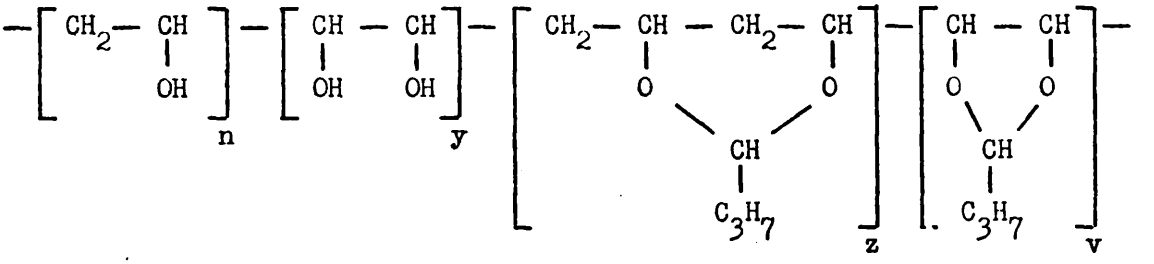
limited to the study of monomer unit distribution in copolymers of different origins which contained no more than 30%, W/W of acetate groups. It was found that the melting points (Tm), of the copolymers were not a simple function of the composition but depended upon the method of preparation. Partial saponification of PV-OAc with sodium hydroxide leads to high melting, ordered copolymers, and reacetylation of PV-OH leads to low melting, random copolymers. Catalytic alcoholysis of PV-OAc yields copolymers intermediate in melting point and order. Similar investigations were made by S.S. Mnatsakanov and his co-workers [46] using DTA technique to study the chemical structure of V-OAc/V-OH copolymers.

D. Vinyl Alcohol/Vinyl Butyral Copolymers. The thermal stability of PV-OH/aldehyde condensates, particularly poly(vinyl butyral), (PVB),

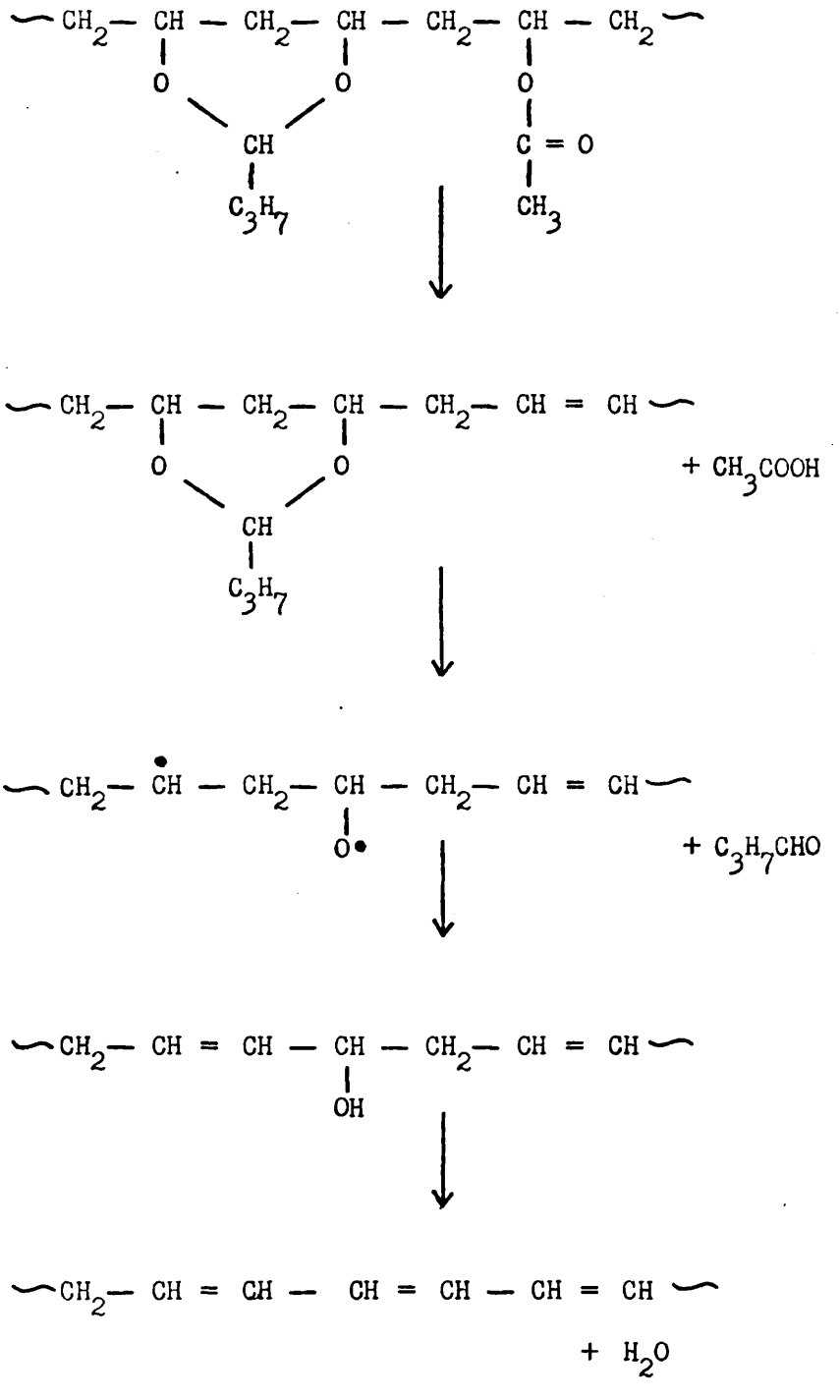


has been of considerable interest. H.C. Beachell, P. Fotis and J. Hucks [47], E.I. Kirillova and E.N. Matveeva [48] studied their thermo-oxidative degradation by the infra-red method in conjunction with weight loss, colour development, and chemical analysis. The reports published about the photo, gamma radiation and thermal degradation [49-52] and also about the stabilisation [53] and pyrolysis [54-56] of PVB describe studies of degradation at 100-800°C by gas chromatography, I.R. and U.V. spectroscopy. Popova and Shuvalova [49] studied the photo and thermal aging of poly vinyl-ethylal and PVB. They showed that in the thermal decomposition of PVB in air at 150°C there was a decrease in the concentration of OH, CH,

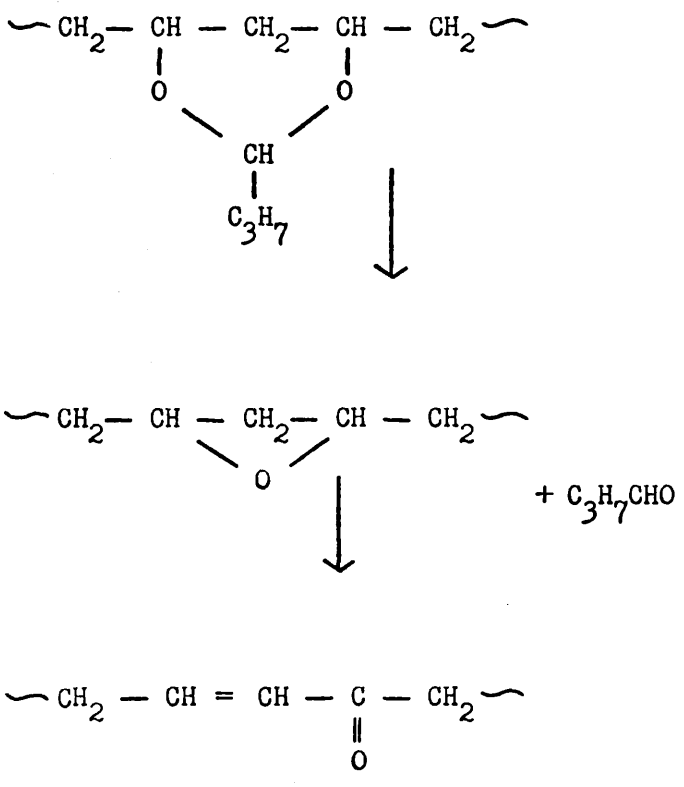
and C-O- groups and an increase in the concentration of -C=O groups (a complex absorption band appeared in the I.R. spectra at about 1730 cm^{-1} due to the formation of ketone and ester groups). O.M. Klimova and co-workers [57] used I.R. spectroscopy to study the characteristic features of the structure and thermo-oxidative degradation of the butyrals and of the copolymers (compared with PVB) and found that increase in the concentration of butyral groups on the



one hand, and increase in the concentration of α-glycol in the original co-polymer on the other, led to an increase in the heat resistance of the butyrals. V.I. Grachev and co-workers [58] studied the kinetics of thermal-oxidative degradation of PV-OH and PVB having different degrees of substitution and found that an increase in the butyral units in PV-OH reduced the length of the polyene systems formed during heat treatment. The rate of formation of polyene systems and of carbonyls in the PVB greatly depended upon the content of butyral groups and the reaction temperature. In the light of their results [58], they have suggested that degradation of acetals in the presence of oxygen from air proceeds by a radical mechanism [24]. The presence of a series of butyral and vinyl acetate units could result in a degradation progress in which a diene and a single double bond is produced according to the following scheme:-



The ethene-carbonyl formation can be visualised as follows:



There is no data available in literature concerning the thermal degradation of PVB and V-CH/VB copolymers under vacuum conditions. So far there is no clear theory on the mechanism of the thermal degradation of PVB and the related copolymers and kinetic studies of the process are scanty.

5. The Effect of Catalytic Impurities on Thermal Stability.

The thermal stability of polymers is strongly influenced by the presence of impurities. Acid hydrolysis of PV-OAc results in traces of acid in the PV-OH; alkaline hydrolysis of PV-OAc results in contamination of the product by a large amount of sodium acetate. These impurities, if not removed from the polymers by thorough washing can lead to instability of the polymers. Traces of acid left in the PVB prepared from PV-OH could catalyse decomposition.

6. Aim of this Work.

The very rapid and steady progress in the application of PV-OAc, PV-OH, PVB and the intermediate copolymers as commercial materials has naturally stimulated interest in the problems of their synthesis and thermal stability.

The primary aim of this work is to study the thermal degradation mechanisms of V-OAc/V-OH and V-OH/VB copolymers and to compare their thermal behaviour with those of the parent homopolymers.

CHAPTER TWO

EXPERIMENTAL PROCEDURE AND TECHNIQUES OF THERMAL ANALYSIS

1. Materials.

The solvents, acetone, methanol, ethanol and n-butyraldehyde were all A.R. grade.

Poly(vinyl acetate) (PV-OAc), (BDH), molecular weight approximately 45,000, was used as supplied.

Poly(vinyl alcohol) (PV-OH), (BDH), molecular weight approximately 14,000, was used as supplied. Elemental analysis indicated that residual acetate was less than 2%.

NaOH catalyst solutions were prepared as follows:

(a) A standard 0·3M solution of NaOH was prepared by dissolving 1·2 g of NaOH in 100 ml of methanol/H_2O ($^{80}/_{20}$).

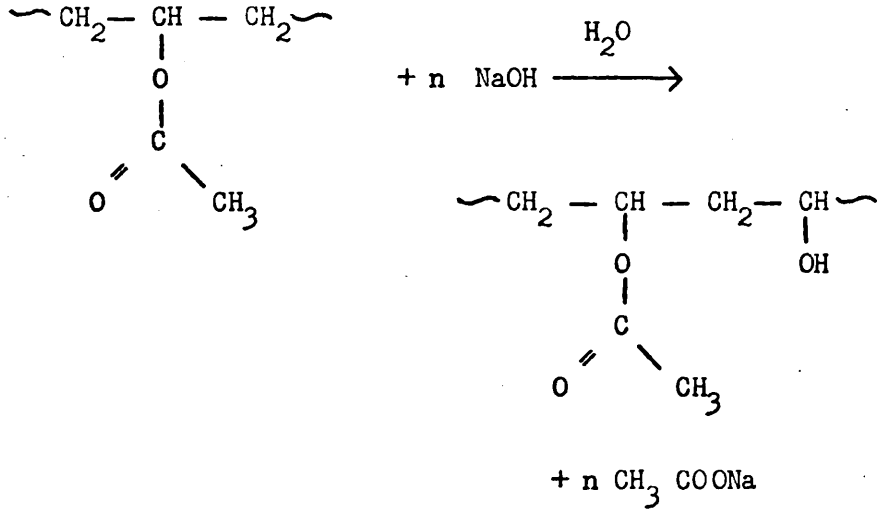
(b) A standard 1M solution of NaOH was used as supplied (Hopkin and Williams. A.R. grade).

2. Preparation of Copolymers of Vinyl Acetate and Vinyl Alcohol.

Copolymers of V-OAc and V-OH were prepared in three ways, by saponification of PV-OAc, by alcoholysis of PV-OAc, and by reacetylation of PV-OH.

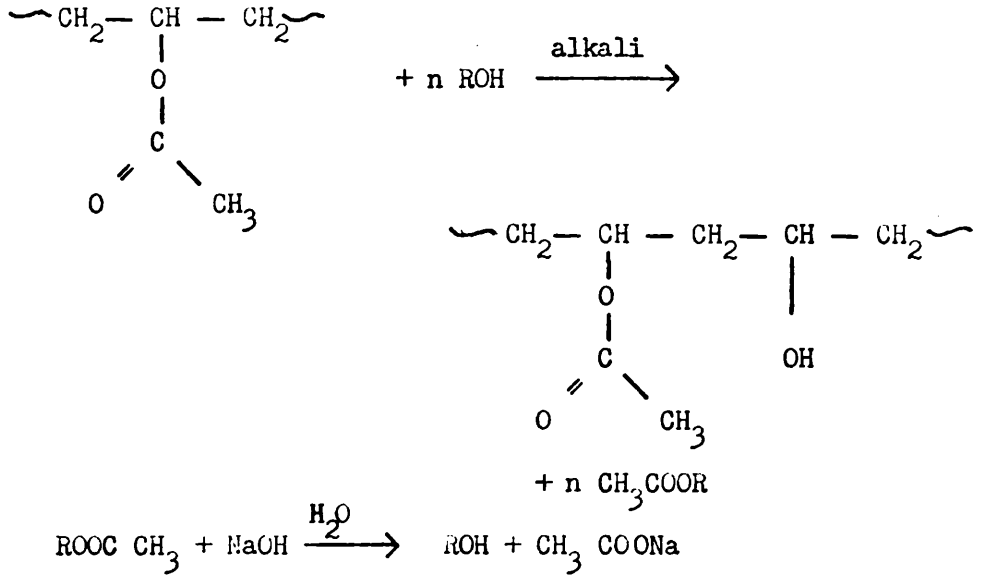
A. Saponification of PV-OAc. A 2% solution of PV-OAc in acetone was prepared. An appropriate amount of aqueous NaOH (1M) was added with stirring and sufficient water to bring the solvent composition to acetone/H_2O, $^{80}/_{20}$. The ultimate extent of hydrolysis of acetate unit

was found to be equivalent to the amount of NaOH used. The reaction mixture was maintained at 35°C and the reaction [59] allowed to go to completion.

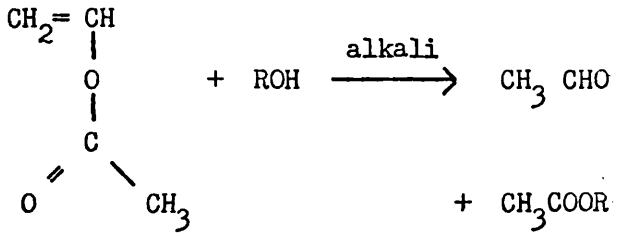


B. Alcoholysis of PV-OAc. The polymer was dissolved in methanol/H_2O, 80/20. A small amount of 0·3M NaOH dissolved in methanol/H_2O, 80/20 was added and the mixture stirred vigorously at 30°C. Alcoholysis was stopped at the appropriate point by the addition of acetic acid.

Skrabal [60] has suggested that the mechanism involves formation of methyl acetate by ester change between methyl alcohol and PV-OAc and that the methyl acetate is then saponified by the alkali:



Skrabal has also suggested that any residual monomer in the polymer is converted to acetaldehyde



The use of the polymer as supplied was justified by checking that reprecipitation of the polymer before use had no effect on the results described in later chapters.

C. Reacetylation of PV-OAc. Random copolymers [15-17] were prepared by reacetylation of PV-OH in mixtures of acetic acid and water. The reaction was performed under reflux ($\sim$100°C) for 24-48 hours. The copolymer composition was controlled by the relative amount of acetic acid and water and the total reaction time.

3. Recovery of Copolymers of V-OAc and V-OH.

PV-OAc alcoholysed or saponified to less than 60% was in the form of a gel and could not be filtered. The Dialysis technique was therefore used to remove the impurities, sodium acetate, sodium hydroxide and methyl acetate. The reaction products were placed in cellophane bags which were mounted in running water for several days.

Polymers hydrolysed above 60% were separated by pouring the reaction mixture into a large amount of water. They were then filtered and washed with mixtures of methanol-water or acetone-water, depending on the reaction medium, until all traces of sodium acetate and other low molecular weight impurities were removed. Finally they were washed

with acetone and dried in a vacuum oven at 60°C for several days.

Only copolymers from the first two methods were studied in detail. Table 2.1. gives the hydrolysis conditions and characteristics.

4. Analysis of Copolymers of V-OAc and V-OH.

The proportions of vinyl acetate and vinyl alcohol units in the copolymers were calculated from elemental analysis using a Perkin Elmer 240 Elemental Analyser, (PV-OH; C,%; H,%; O,% : PV-OAc, C, %; H,%; O, %;). The results obtained by elemental analysis were shown to be in good agreement with results obtained by the following method which was not, however, generally used because of the relatively large amount of copolymer required.

0·5 g of copolymer was dispersed in 20 c.c. pyridine at 60°C. An excess of standard KOH in methyl alcohol was pipetted into the flask. After heating at 60°C for one hour, 100 c.c. of distilled water was added and the sample left at room temperature for approximately sixteen hours. During this time the PV-OH which precipitated during hydrolysis either dissolved completely or became swollen. Excess alkali was titrated with standard HCl. From the alkali consumed, the V-OAc content of the sample was calculated. Analyses were made in duplicate and averaged.

These copolymer compositions were qualitatively confirmed by NMR.

Table 2.1.

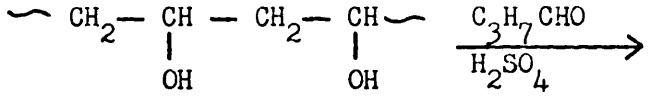
Hydrolysis Conditions and their Characteristics.

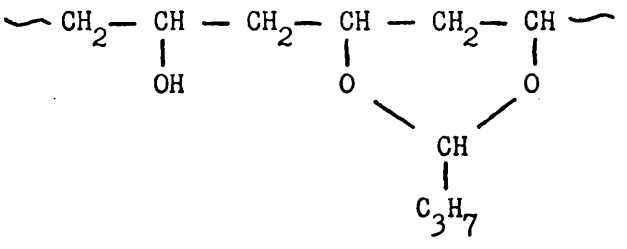
Catalyst	Medium	Catalyst Consumption	By products	Rate Control	Type of residual acetate distribution
alkaline	MeOH $+H_2O$	Small	MeOAc NaOAc	difficult	Blocky
	Acetone + H_2O	Equivalent to PV-OAc unit	Equivalent NaOAc	Easy	Very blocky

5. Preparation and Purification of Copolymers of Vinyl Alcohol (V-OH) and Vinyl Butyral (VB).

PV-OH was used as a starting material for the preparation of copolymers of V-OH and VB.

A homogeneous solution was prepared by warming PV-OH (5 g), methanol (4 ml) and water 41 ml) and conc. H_2SO_4 (0·3% of total weight of reaction mixture) in a three necked flask equipped with a mechanical stirrer. A calculated amount of n-butyraldehyde was added with vigorous stirring over a period of 20 minutes while the internal temperature was raised to about 70°C. 30 ml of hot water at approximately 70°C was then added over a period of 15-20 minutes. The resulting mixture was agitated for a further 10 minutes, and a small amount of conc. H_2SO_4 dissolved in 10 ml H_2O added. The reaction mixture was stirred for a further hour, and the resulting product filtered and washed repeatedly with water and dilute alkali to remove all traces of acid which could catalyse decomposition.





Copolymers were carefully washed with water and dried in a vacuum oven at 80°C for several days.

Copolymer compositions were calculated from elemental analysis.

6. Thermal Volatilisation Analysis (TVA).

TVA has been the subject of a number of Publications [61-66] and is now a well established technique of thermal analysis.

A. Principle of TVA. TVA measures the rate at which volatile products are evolved from a degradating substance over a particular temperature range. A polymer sample is heated at a linear rate ($10^{\circ}C$/Min) in a continuously evacuated system. A pressure develops due to volatile products of degradation which distil from the hot zone to a cold trap. This pressure is measured by a Pirani gauge and is continuously recorded on a pen recorder. The resulting thermogram describes Pirani response as a function of temperature.

The heating zone consists of a Perkin Elmer F 11 oven controlled by a linear temperature programmer, which can heat the sample isothermally or from ambient temperatures up to $500^{\circ}C$ at linear rates, ranging from 1° to $40^{\circ}C$ per minute. Fig. 2:1 illustrates the basic TVA system.

The oven arrangement is shown in Fig. 2:2. The temperature of the oven is measured by a chromel-alumel thermocouple B, placed at the base of the pyrex degradation tube A. The upper portion of the tube and the greased flange joint is cooled by the water jacket C during the course of an experiment.

B. Differential Condensation TVA. The simple TVA system described above has been developed further to allow differential condensation of products [64,65]. This development is represented in Fig. 2:3. The degradation products pass along four equivalent routes, each with a cold trap, operating usually at four different temperatures namely, 0°, -45°, -75° and $-100^{\circ}C$ respectively. A Pirani gauge is positioned between each of the traps and a common liquid nitrogen trap,

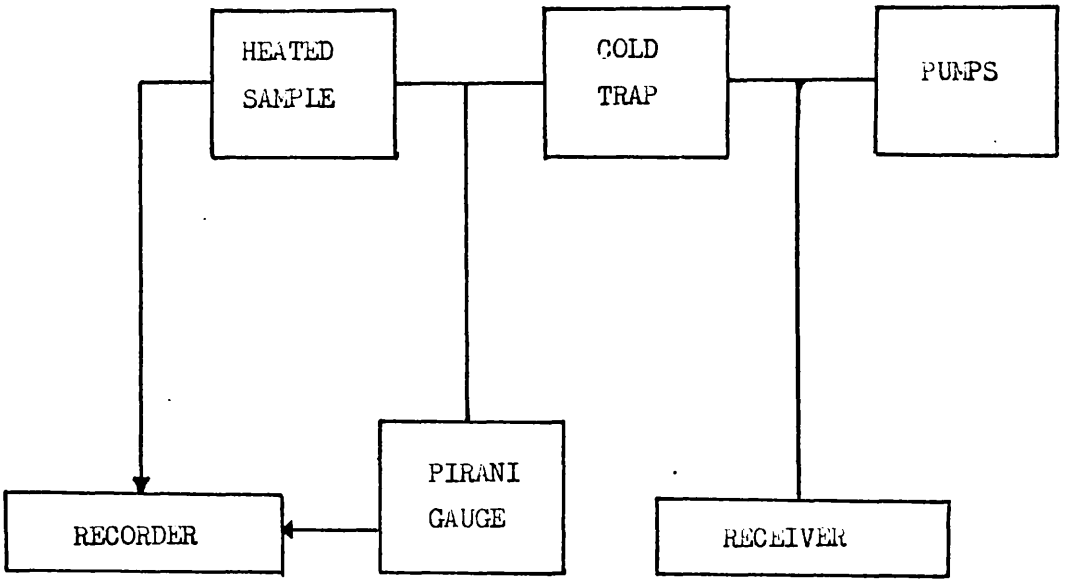


Fig. 2:1 Schematic layout of basic TVA apparatus

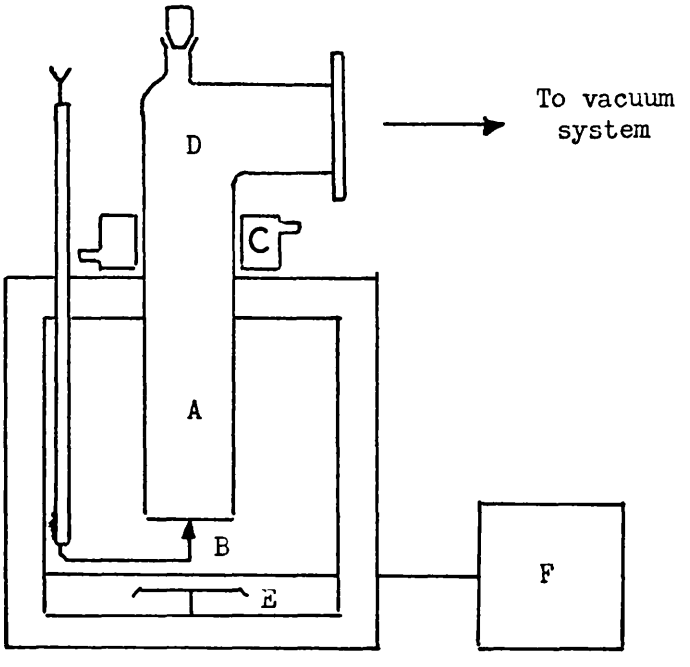


Fig. 2:2 Oven arrangement for TVA

A Degradation tube

B Chromel-alumel thermocouple

C Cooling jacket

D Removable socket joint

E Oven fan

F Temperature programmer

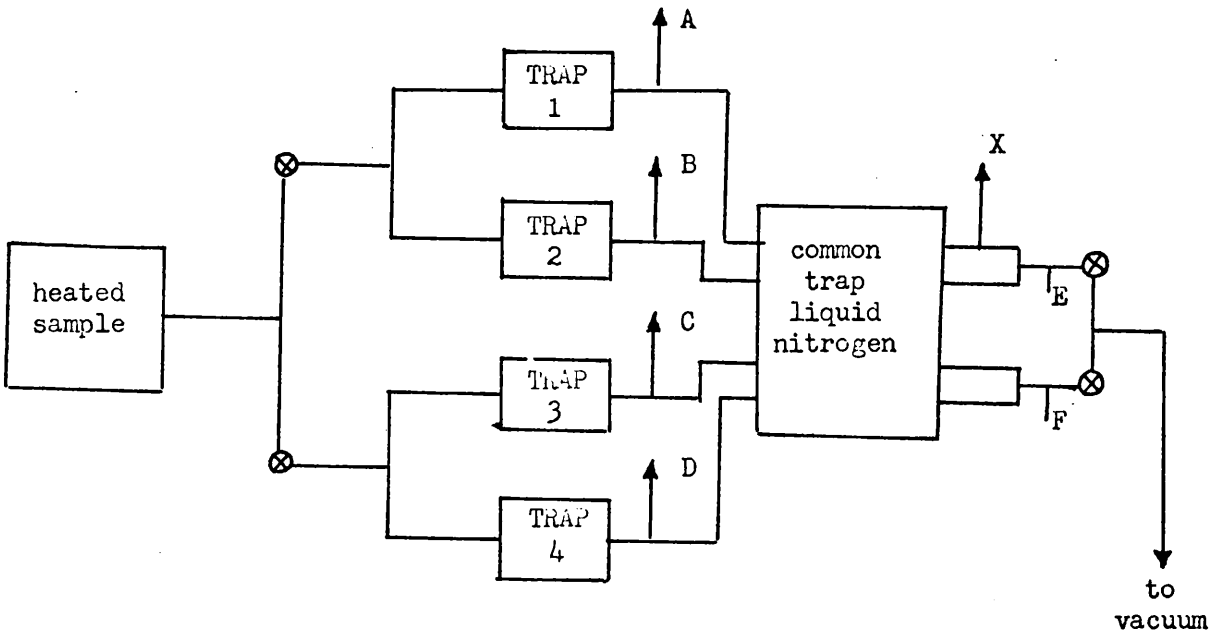


Fig. 2:3

Thermal working temperatures (°C): 0, -45, -78, -100

A, B, C, D are Pirani gauge heads

E, F are sample receiving tubes as IR gas cell

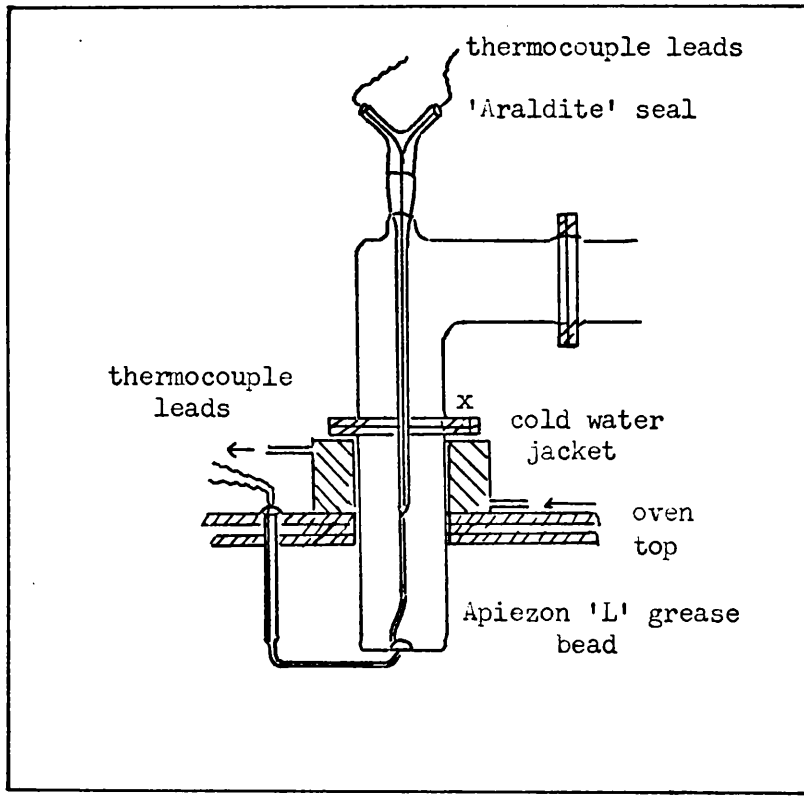


Fig. 2:4 Assembly for temperature calibration.

and a fifth Pirani gauge is positioned after this latter trap. A multi gauge head unit transmits the responses from the five Pirani gauges to a twelve channel recorder, where they are recorded together with the output from the oven thermoccuple. Thus volatile degradation products from the sample may be fractionated according to their condensability or non-condensability at each of the five temperatures and a DCTVA thermogram is thus obtained.

C. Temperature Calibration of TVA. The actual temperature of the interior of the base of the degradation tube is lower than the temperature recorded during an experiment which is that of the oven thermocouple B, shown in Fig. 2:2. This thermal lag is a function of temperature, heating rate, particular degradation tube being used and position of the oven thermocouple. The internal base temperature may be obtained by calibration with a second internal thermocouple whose junction is surrounded at the point of contact between glass and metal by a small bead of Apiezon "L" grease, to improve thermal contact and to stimulate molten polymer [63] (see Fig. 2:4).

The temperature differential between tube and oven thermocouple is plotted as a function of oven temperature and heating rate in Fig. 2:5.

(a) Limitations of TVA. Only those products which are sufficiently volatile to reach the Pirani filament are recorded in a TVA thermogram. This means that not all the processes detected by thermogravimetry can be detected by TVA. In this respect TVA is similar to other gas evolution analysis, such as MTA or pyrolysis/glc. However, a TVA thermogram is obtained because of the great sensitivity of the Pirani gauge, even if only a small proportion of the weight of the material is lost.

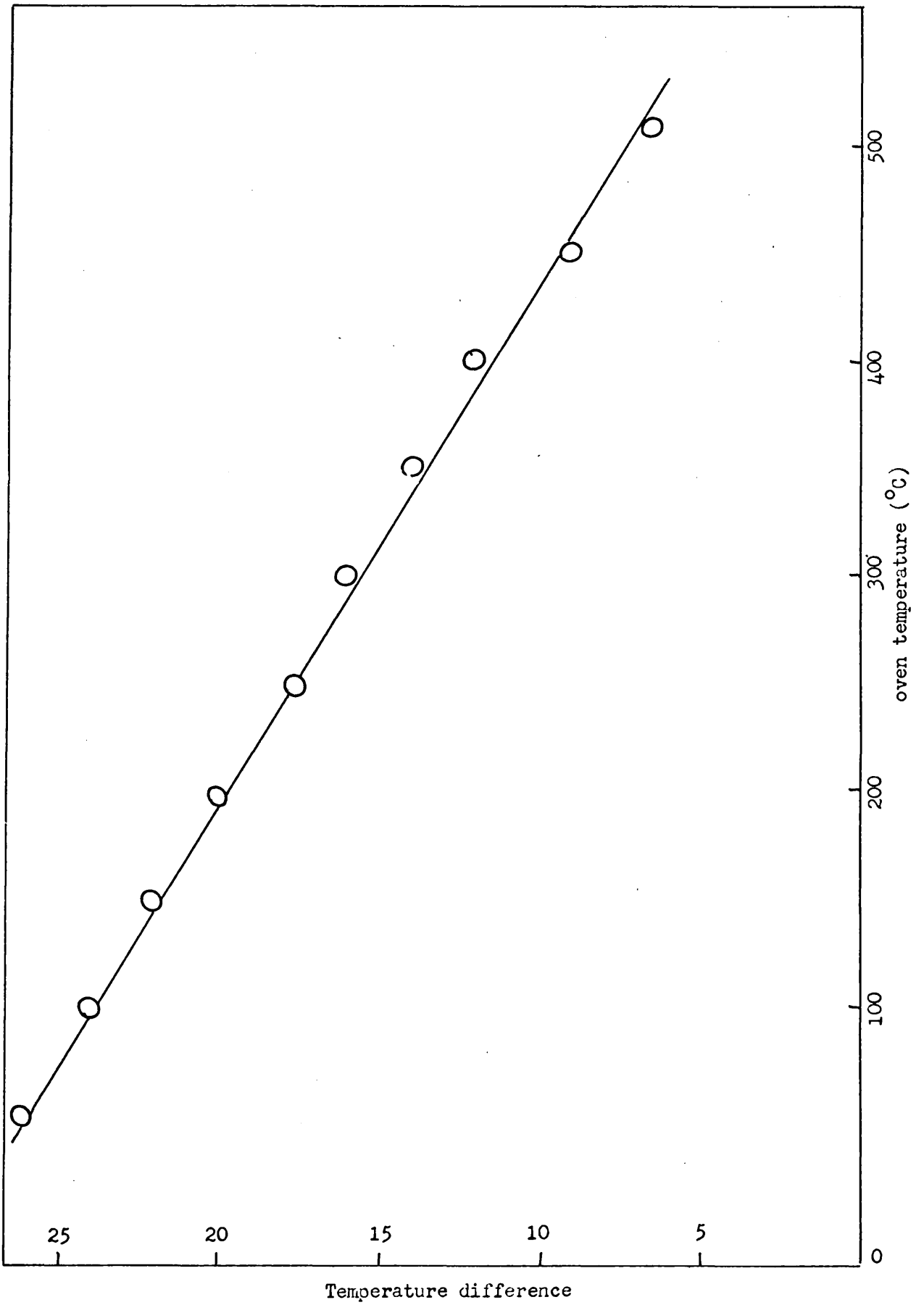


Fig. 2:5 Temperature calibration graph

As with TGA kinetic parameters can be obtained, but in this study copolymers of vinyl alcohols were found to present a complicated degradation pattern, so TVA has in this instance been used only for qualitative purposes.

(b) Advantages of TVA. In TVA the temperature gradients within the sample are minimised as the sample is heated either in the form of a very thinly distributed powder or a film, and the temperature of the sample can be accurately measured because of the massive degradation tube. Furthermore, the large area available for the sample and the continuous and efficient removal of the volatiles from the sample are efficient factors which tend to reduce the chance of diffusion controlled processes and secondary reactions of products occurring in TVA.

D. Product Analysis from TVA. During the investigation of polymer breakdown, interest may centre on one or more of the three main products fractions:- the products which are volatile at ambient temperature, the products (often waxy or oily) which are volatile only at degradation temperature and the solid residue of degradation. In the TVA apparatus these products are conveniently separated as follows.

(i) Volatile products, passing through the vacuum system, which may be further separated by differential condensation.

(ii) Products which condense out on the limited area of the upper part of the degradation tube which is cooled by a cold water jacket C Fig. 2:2. This is described as the cold ring fraction (CRF).

(iii) The solid residue left on the flat base of the degradation tube.

Greatest interest is usually focussed on fractions (i) and

(iii). Fraction (iii) may be examined by infra-red or ultra-violet spectroscopy at the end of the experiment or at intermediate intervals by interrupting the experiment. If soluble, it can be subjected to molecular weight determinations. Products condensed in the cold traps, fraction (i) may be isolated and then distilled into a receiver suitable for subsequent analysis.

Degradation products which are non condensable in liquid nitrogen, for example, methane, carbon monoxide or hydrogen, and which pass through the cold traps are lost in the continuously evacuated system but may be isolated if a closed system is used.

The sample size was 30 mg for each polymer. The polymer samples were degraded to 500°C at a heating rate of 10°C/min under normal conditions of TVA.

7. Sub-Ambient TVA.

A. Principle of Sub-Ambient TVA. The technique is based on the principle that if a frozen mixture of different compounds is allowed to warm slowly under high vacuum conditions, and with continuous pumping, fractionation occurs as the separate components of the mixture evaporate at different temperatures.

B. Description of the Apparatus. The apparatus is described schematically in Fig. 2:6. Sample preparation and heat assembly are the same as for conventional TVA, condensable volatiles from the degrading sample being collected in a main cold trap. On completion of degradation with traps A, C closed and B open, the condensable products are distilled into the benzene trap frozen to −196°C (detail in Fig. 2:7). With tap B now closed and tap C open, ie. under conditions of

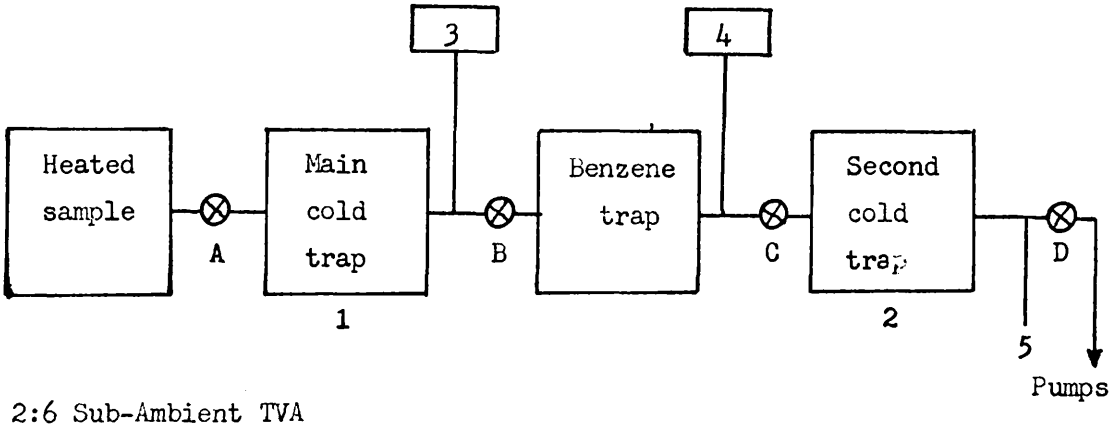


Fig. 2:6 Sub-Ambient TVA

1, 2 : liquid nitrogen traps

5 : Receiving vessel (sample collection point)

3, 4 : Pirani gauges

A, B, C, D : Stopcocks

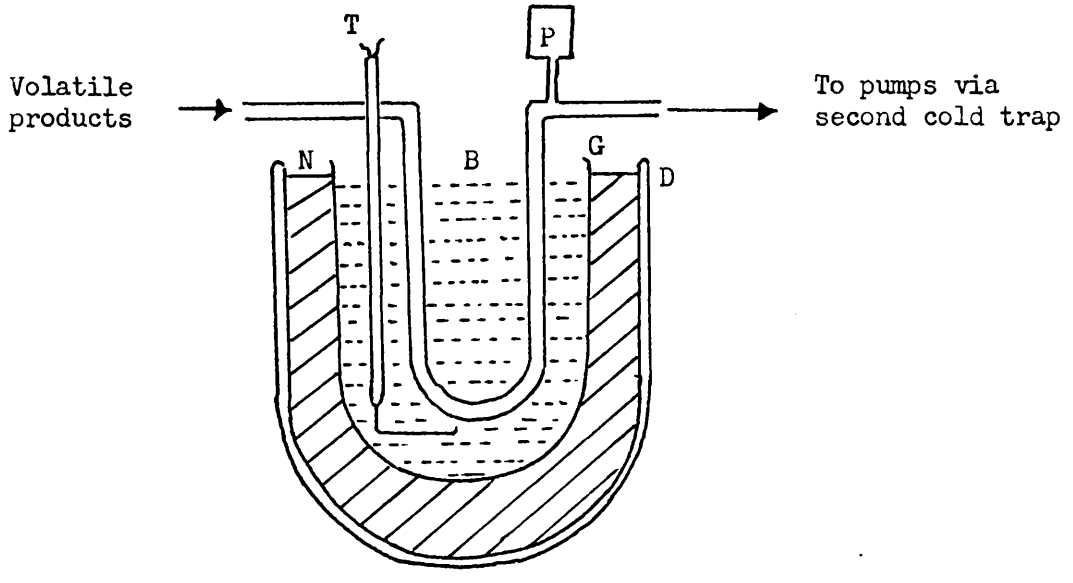


Fig. 2:7 Detail of Benzene trap.

B : Frozen benzene

G : Pyrex glass flask

D : Dewar vessel

P : Pirani gauge

T : Thermocouple

N : Liquid nitrogen

continuous pumping, the outer liquid nitrogen trap is removed from around the benzene, allowing it to warm up very slowly by heat transfer from the surroundings. In practice, this occurs reproducibly so that a controlled (although non-linear) rate of temperature increase is obtained. The separate products distil into cold trap 2, and a thermocouple is used to measure the temperature at which each distilling product exerts its maximum pressure on the Pirani gauge, 4, whose output is transmitted to a recorder.

C. Collection of Separated Products. Products responsible for separate peaks in the sub-ambient TVA thermogram can be collected separately in the following way.

The benzene trap is allowed to warm as described, but on production of the first peak on the thermogram, tap C is closed and the benzene re-frozen to $-196^{\circ}C$. With taps C and D closed, the product responsible for the first peak can now be distilled into a suitable collecting vessel and removed. After re-evacuation of the second trap, it is again cooled to $-196^{\circ}C$, tap C is opened, the benzene allowed to warm again and the product responsible for the next peak collected in a similar manner. In this way, products which give rise to separate peaks on the thermogram may be separated.

This separation technique was especially helpful in the present work in obtaining clearer i.r. identification evidence for the presence of products whose i.r. absorptions were to a large extent undetectable in an i.r. spectrum of the total volatile products.

8. Thermal Gravimetric Analysis (TGA).

TG is a well established thermal analysis technique in which the

weight of a sample is continuously recorded while the temperature is raised linearly. T.G. curves quickly provide a measure of the total extent of degradation but require to be differentiated to obtain rates of reaction. The temperatures at which rate maxima occur are much less accurately measured than in TVA. A more detailed comparison between the two techniques is given by McNeill and Neill [66].

T.G. curves were obtained from a Du Pont 900 Differential Thermal Analyser with accessory 950 TG Module. The thermobalance was of the null deflection type employing a photoelectric system to detect and compensate for movements of the quartz beam from which the platinum sample pan was suspended. The heat was supplied by a programmed furnace into which the silica tube enclosing the balance beam, sample pan and thermocouple slid horizontally. CAHN-RG electrobalance was used for TGA studies under vacuum.

5 mg and 25 mg samples were heated in a dynamic nitrogen atmosphere flowing at 60 ml/min and in vacuum respectively at a normal heating rate of 10°C/min.

9. Differential Theraml Analysis (DTA).

DTA thermograms were obtained using a Du Pont 900 instrument. DTA is a technique for studying the thermal behaviour of materials as they undergo physical or chemical changes during heating or cooling. A 10 mg sample was heated at 10°C/min in a dynamic nitrogen atmosphere flowing at 60 ml/min.

10. Spectroscopic Measurements.

Infra-red spectra were obtained using a Perkin Elmer 257

Grating Spectrophotometer. Insoluble residues were measured as KBr discs and soluble residues as films cast on salt plates. Products from TVA were examined as thin films on NaCl discs or in the gaseous phase according to their volatility.

NMR spectra were measured using a JEOL C 60 HL instrument for the determination of copolymer composition. Spectra of PV-OAc, PV-OH and the intermediate copolymers were measured in $(CD_3)_2CO$, D_2O and a mixture of D_2O and CD_3OH respectively.

11. Viscosity Measurements.

Viscosity measurements of PV-OAc in different solvent mixtures were carried out in a Ubbelohde viscometer at 25°C. The specific viscosity of a solution is defined by the relationship,

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{t - t_o}{t_o}$$

where η = Viscosity of the solution

η_o = Viscosity of the solvent

t = Flow time for solution

t_o = Flow time for solvent

The intrinsic viscosity $[\eta]$ is obtained by extrapolating a plot of $\eta_{sp}/_c$ against concentration C to zero concentration. Concentration is expressed in grams per decilitre ($g/_{dl}$, $g/_{100}$).

12. Measurement of Molecular Weight.

Number average molecular weights were determined osmotically using a Hewlett-Packard 501 High Speed Membrane Osmometer with cellophane

300 membranes and using toluene as solvent. Osmotic pressure measurements were made at a series of polymer concentrations applying the equation,

$$\frac{\pi}{C} = \frac{RT}{M_n} + bC$$

A plot of π/C Vs C was drawn. By linear extrapolation of the graph to infinite dilution, the number average molecular weight was determined from the relationship,

$$\left(\frac{\pi}{C}\right)_{C \rightarrow 0} = \frac{RT}{M_n}$$

CHAPTER THREE

THE HYDROLYSIS OF POLY(VINYL ACETATE)

1. Introduction.

The hydrolysis of PV-OAc has been carried out in methanol/H_2O and acetone/H_2O solutions. These were described in Chapter Two as alcoholysis and saponification respectively and this nomenclature will be continued throughout this work.

In the present study the effect of a number of variables on the hydrolytic conversion of PV-OAc to PV-OH has been investigated. These include the effect of different catalysts, temperature, and the nature of solvent.

Although alkaline hydrolysis is much more rapid than acid hydrolysis the former has been preferred for the present study because the latter is more likely to give some ether linkages in the chain by a mechanism involving the loss of a molecule of water from adjacent hydroxyl groups. Minsk, Priest and Kenyon [67] have shown that the two processes are superficially similar, although the mechanisms are rather different [68].

Lee and Sakurada [69] studied the alcoholysis of PV-OAc in methanol/H_2O solutions and found it to be second order, first order with respect to each of the reactants poly(vinyl acetate) and catalyst, but independent of the polymer chain length. In acetone/H_2O mixtures, it was found that the rate increased with increasing degree of hydrolysis which has been associated with the absorption of the alkali catalyst at the hydroxyl groups adjacent to the acetate groups [70-74].

It has been concluded that the initial rate constant, k_o, in both media is independent of the concentration of PV-OAc.

All the experiments reported in this chapter have been carried out using the same polymer and catalyst concentrations, namely, 0·23M and 0·3M respectively.

2. Results and Discussion.

A. Effect of Temperature on the Rate of Reaction.

(a) Alcoholysis in Methanol/H_2O, $^{70}/_{30}$. Fig. 3:1, derived from the data in Table 3.1 illustrates the effect of temperature on the course of the reaction in $^{70}/_{30}$, methanol/H_2O solution. As expected the initial rate increases with temperature, but in a polymer system of this kind the normal activation effect may be modified somewhat by the fact that the medium changes with temperature in the sense that the molecules will be rather less coiled at higher temperature and the individual acetate groups thus more liable to attack.

The relatively high initial rate decreases rapidly in the later stages. Although this will be principally due to decreasing concentrations, it has been suggested [67] that the reverse reaction may contribute as the concentration of methyl acetate increases. In addition the shape of the reaction curve may be effected by the progressive increase in the hydroxyl content of the polymer, which may cause a change in the solvent-solute relationship as the reaction progresses. Steric effects of this kind have been shown to be responsible for the accelerations which have been noted in other investigations of alcoholysis [75] and hydrolysis [76] of esters of poly basic acids.

The second order plots, shown in Fig. 3:2, were derived from

Table 3.1.

Alcoholysis of PV-OAc in Methanol/H_2O, $^{70}/_{30}$ at various temperatures.

(PV-OAc, 0·23M; NaOH, 0·3M)

Temperature (°C)	Time (Min)	% Alcoholysis	Temperature (°C)	Time (Min)	% Alcoholysis
26	5	29	36	5	22·7
"	15	41·45	"	10	53·896
"	23	50·828	"	18	63·27
"	32	57·68	"	23	66·67
"	42	61·57	"	30	69·9
"	57	65·65	"	42	72·13
"	67	67·7	"	50	73·496
"	82	70·4	"	60	73·92
30	5	31·9	45	5	27·1
"	13	46·56	"	8	56·79
"	21	56·45	"	13	66·17
"	31	63·26	"	18	70·43
"	38	65·48	"	23	72·3
"	48	68·21	"	28	73·66
"	63	70·77	"	33	74·35
"	78	72·64			

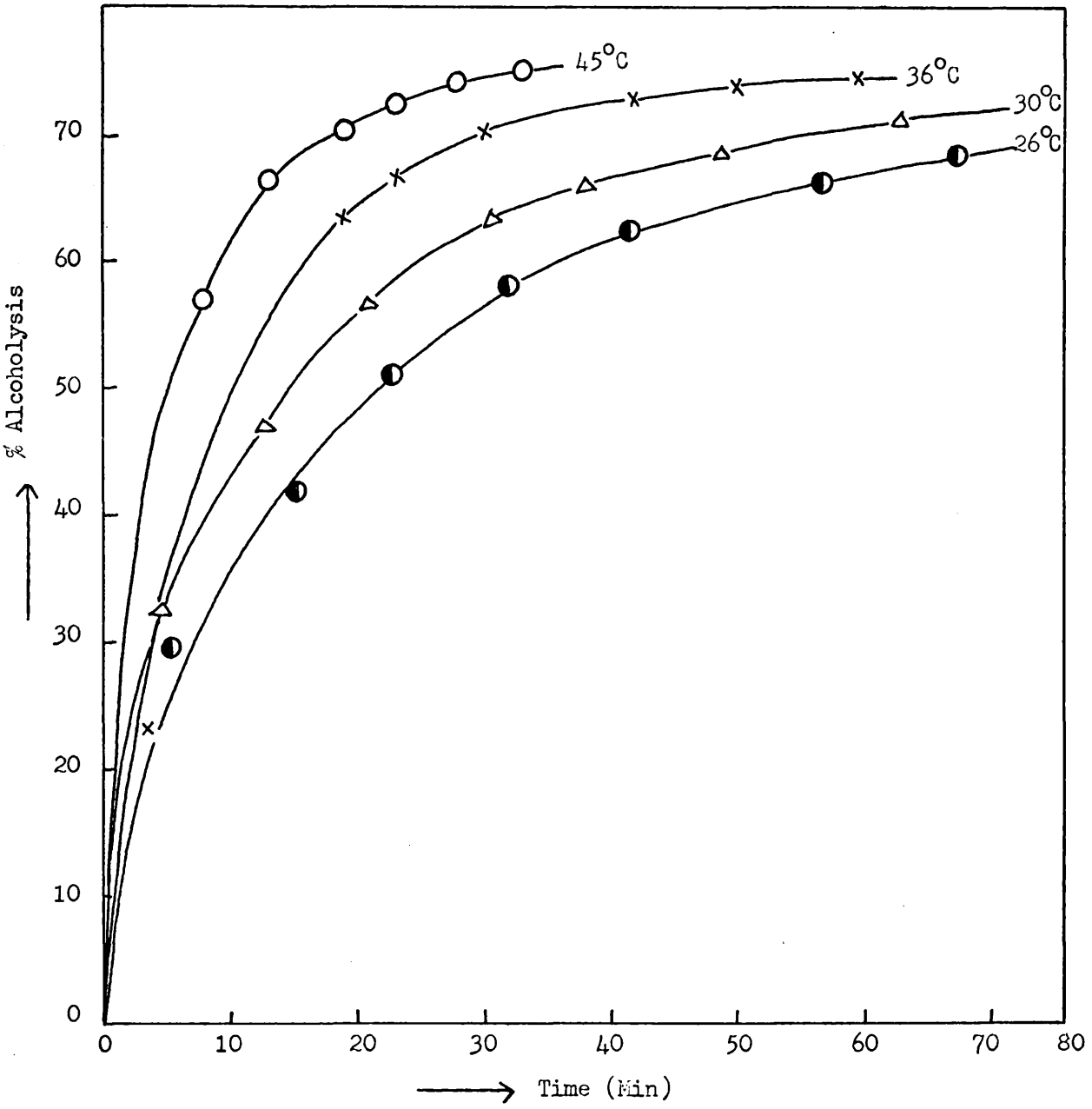


Fig. 3:1 Alcoholysis of PV-OAc in methanol/H_2O, $^{70}/_{30}$ as a function of time at different temperatures.

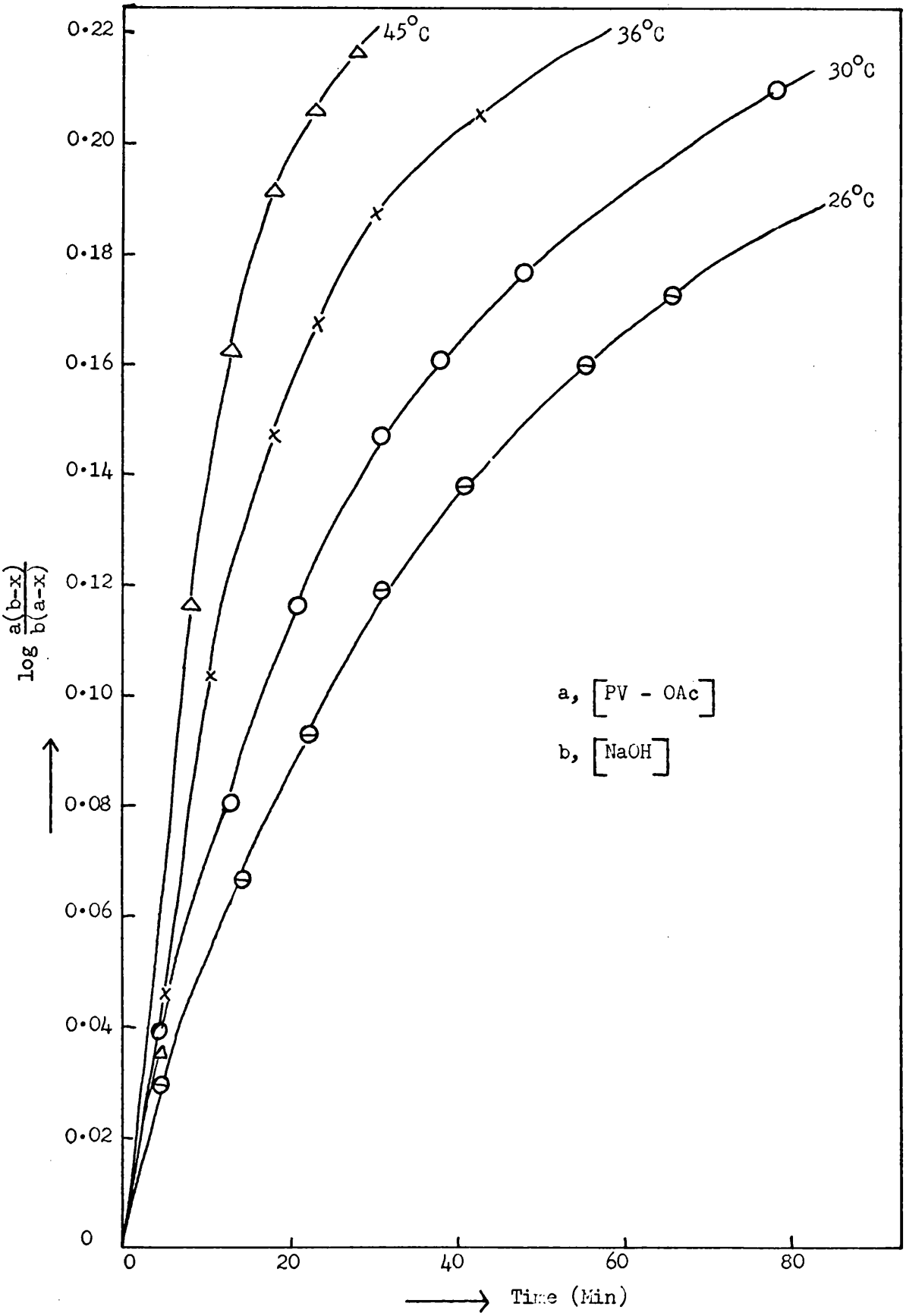


Fig. 3:2 Second order plots of methanolysis of PV-OAc at different temperatures.

Table 3.2.

Rate Constants, k_o, for the Alcoholysis of PV-OAc by NaOH (0·3M) in CH_3OH/H_2O, $^{70}/_{30}$.

Temperature (°C)	k_o (l/mole min)
26	$19{\cdot}76 \times 10^{-2}$
30	$24{\cdot}75 \times 10^{-2}$
36	$34{\cdot}58 \times 10^{-2}$
45	$44{\cdot}24 \times 10^{-2}$

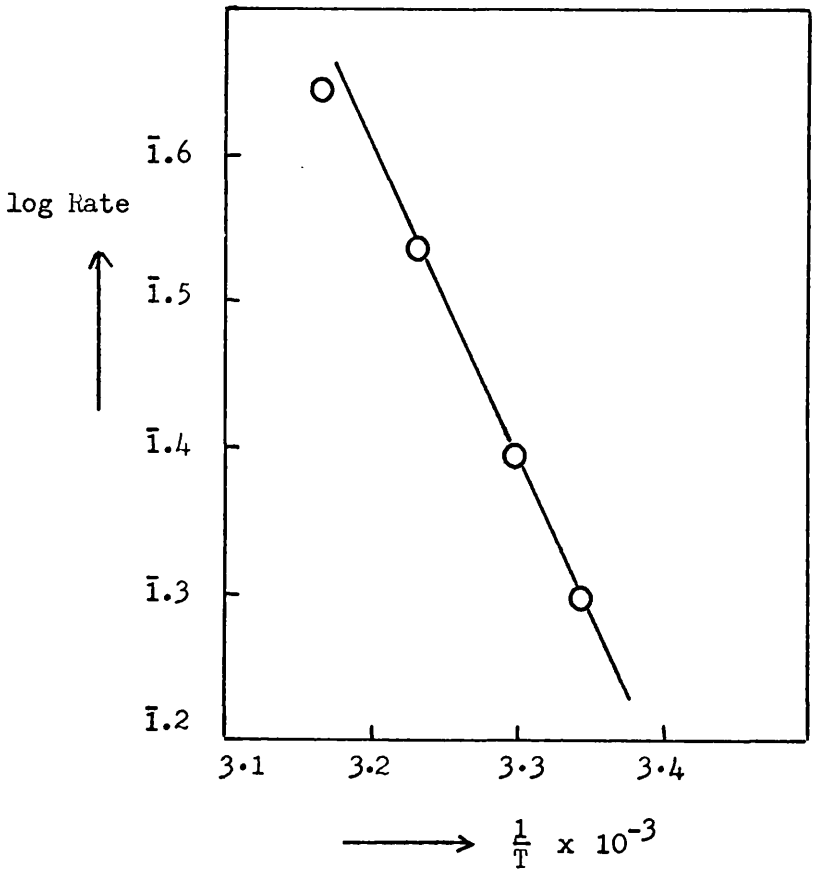


Fig. 3:3 Determination of Activation Energy for PV-OAc in methanol/H_2O, $^{70}/30$ by plotting values of log Rate versus $^{1}/_{T}$ o_K (the Arrhenius plot).

the data in Table 3.1. These are not straight lines presumably due to the complicating factors mentioned in the last paragraph but, accepting Lee and Sakurada's finding [69] that the reaction is second order in the initial stages, rate constants were calculated from the initial slopes of the curves in Fig. 3:2. The rate constants are given in Table 3.2 and from the Arrhenius plot in Fig. 3:3, a value of 9·152 $K cal/_{mole}$ for the energy of activation may be calculated.

(b) Alcoholysis in Methanol/H_2O, $^{50}/_{50}$. PV-OAc is only partially soluble in methanol/H_2O, $^{50}/_{50}$, forming a cloudy solution. Fig. 3:4, derived from the data in Table 3.3, shows the progress of the reaction at different temperatures. The course of the reaction is clearly autocatalytic and temperature dependent. The autocatalytic characteristics may be due to the fact that in the initial stages of the reaction the polymer molecule is in a state of tighter coiling, which hinders chemical reaction. As the reaction proceeds the polymer becomes more soluble. The polymer chains thus become more extended and the ester groups more accessible.

(c) Saponification in Acetone/H_2O, $^{50}/_{50}$. Fig. 3:5 illustrates the effect of temperature on the course of the reaction in acetone/H_2O, $^{50}/_{50}$ solution. As expected the rate increases with temperature. The polymer is also only partially soluble in the solvent and the autocatalytic characteristics are accounted for in the same terms as those in the methanol/H_2O, $^{50}/_{50}$ solvent discussed above. In both cases the increase in the hydroxyl content of the polymer during the course of the reaction may also play a part in causing autocatalytic characteristics by changing the solvent-solute relationship in such a way as to increase in the hydrolysis rate.

Table 3.3.

Alcoholysis of PV-OAc in Methanol/H_2O, $^{50}/_{50}$ at various temperatures.

(PV-OAc, 0·23M; NaOH, 0·3M)

Temperature (°C)	Time (Min)	% Hydrolysis	Temperature (°C)	Time (Min)	% Hydrolysis
25	5	0·377	30	5	0·38
"	13	2·93	"	12	2·93
"	20	4·13	"	21	21·34
"	28	10·09	"	25	55·94
"	40	35·66	"	30	66·50
"	50	54·75	"	36	70·94
"	58	61·224	"	42	72·98
"	69	67·53	"	55	74·68
"	79	69·75	45	5	1·57
"	90	72·138	"	10	34·13
"	100	73·84	"	17	57·64
			"	22	63·27
			"	28	70·598
			"	35	74·177
			"	40	74·86

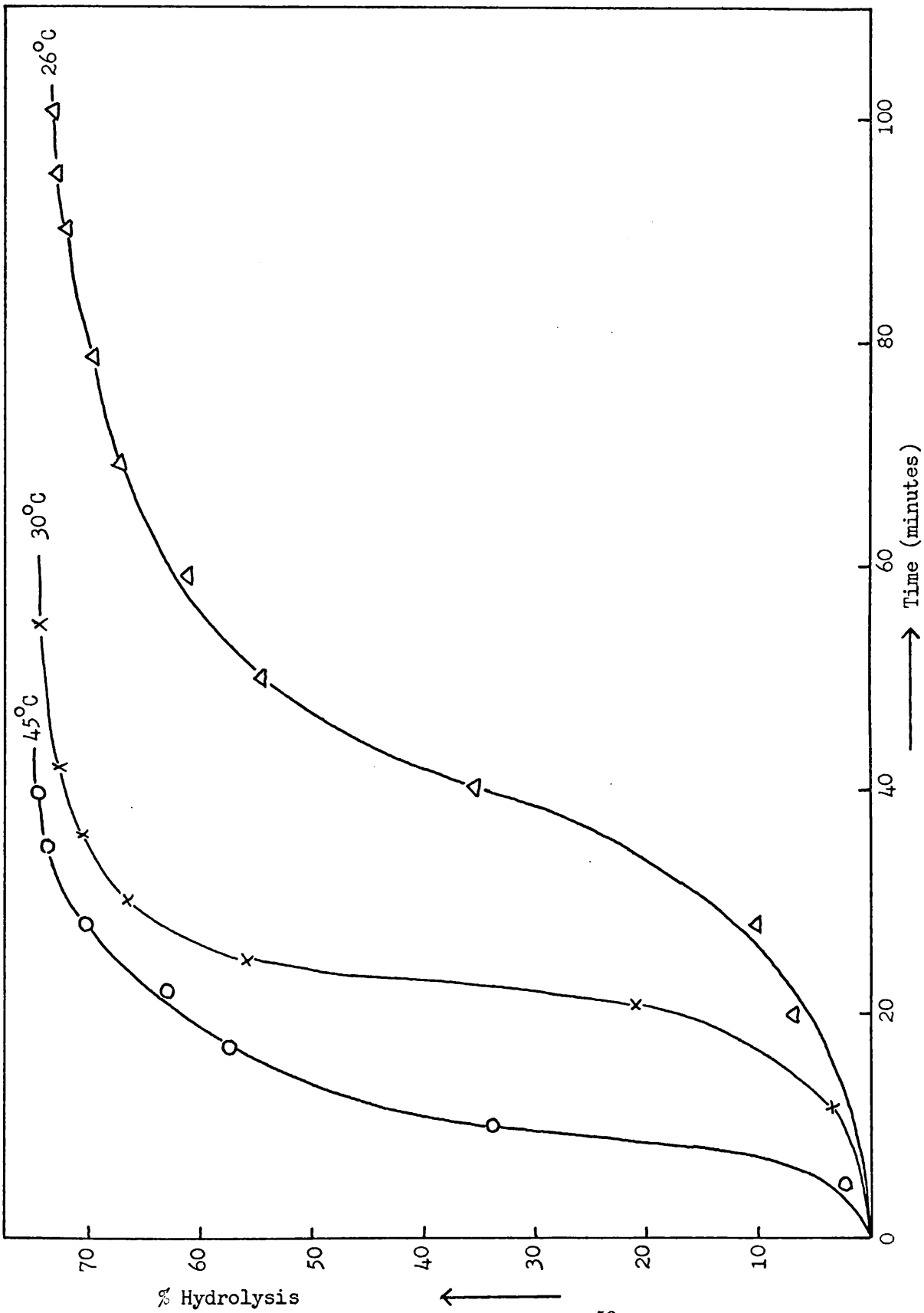


Fig. 3:4 Methanolysis of PV-OAc in Methanol/H_2O, $^{50}/_{50}$ as a function of time at different temperatures.

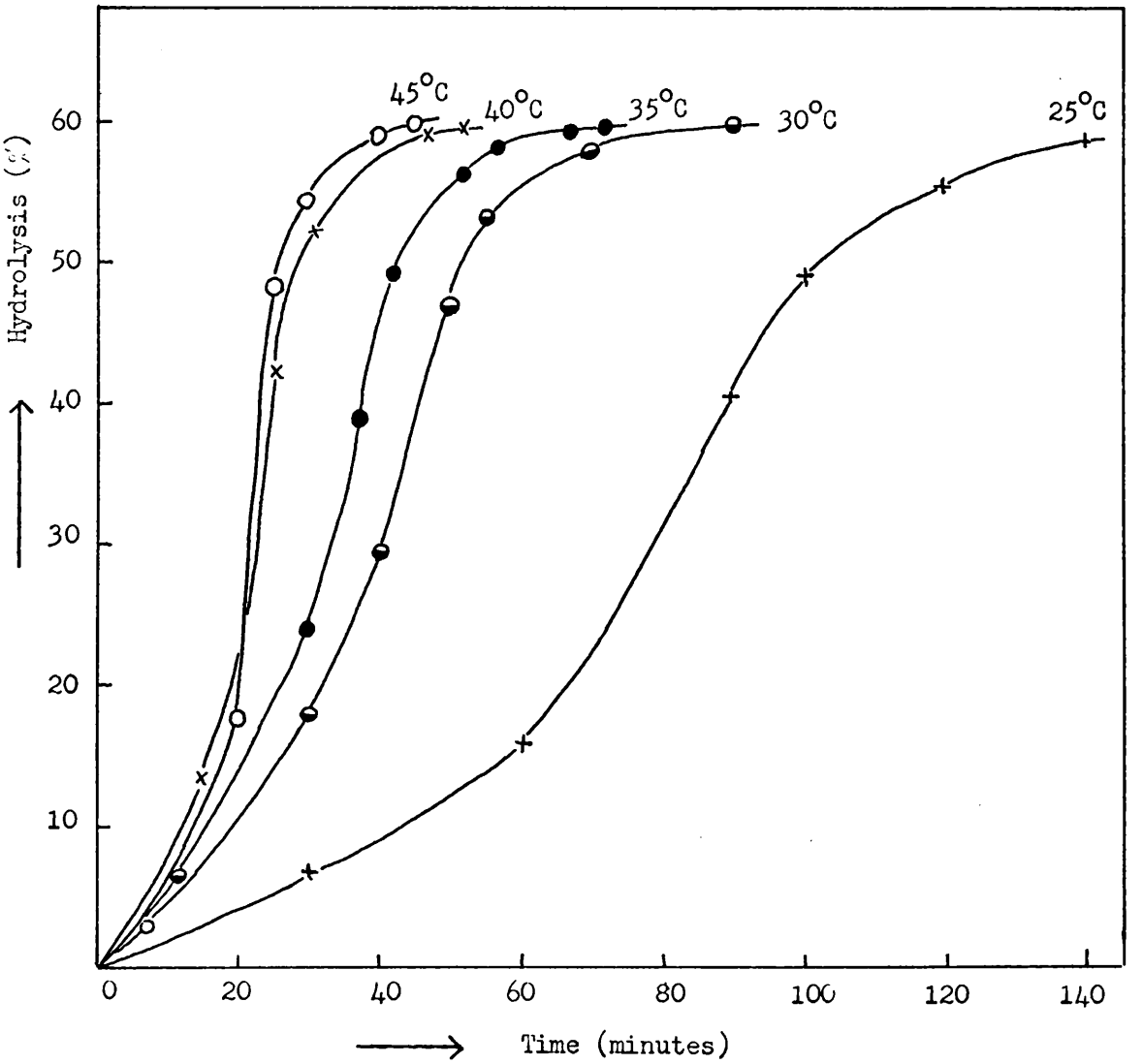


Fig. 3:5 Saponification of PV-OAc in Acetone/H_2O, $^{50}/_{50}$ as a function of time at different temperatures.

B. Influence of the Composition of the Solvent Mixture on the Rate of Reaction.

(a) Saponification in Acetone/H_2O. Fig. 3:6, derived from the data in Table 3.4 shows the effect of the composition of the solvent mixture on the course of the reaction. The polymer was soluble, forming a clear solution, in the $^{70}/_{30}$ and $^{65}/_{35}$ solvent mixtures. It becomes progressively less soluble as the proportion of water is increased. As in the methanol/H_2O system it is clear that autocatalytic properties appear when the polymer is insoluble in the solvent and may be accounted for as before principally in terms of chain coiling. For the reactions in the $^{70}/_{30}$ and $^{65}/_{35}$ solvent mixtures, second order plots have been obtained and rate constants calculated as before. These are present in Fig. 3:7 and Table 3.5 respectively.

An additional effect of solvent composition is suggested by Katchalsky's [77] observations on the hydrolysis of pectin. He suggested that the lower rate of hydrolysis in water rich system may be attributed to the formation of carboxylate groups, which dissociate into ions. The polymer molecules thus become negatively charged and repel hydroxyl ions so that the hydrolysis reaction is depressed. With increasing concentration of acetone the dissociation of carboxylate groups become less extensive and the effect of the electrostatic repulsion is suppressed so that the catalyst concentration in the close proximity of polymer molecules is higher.

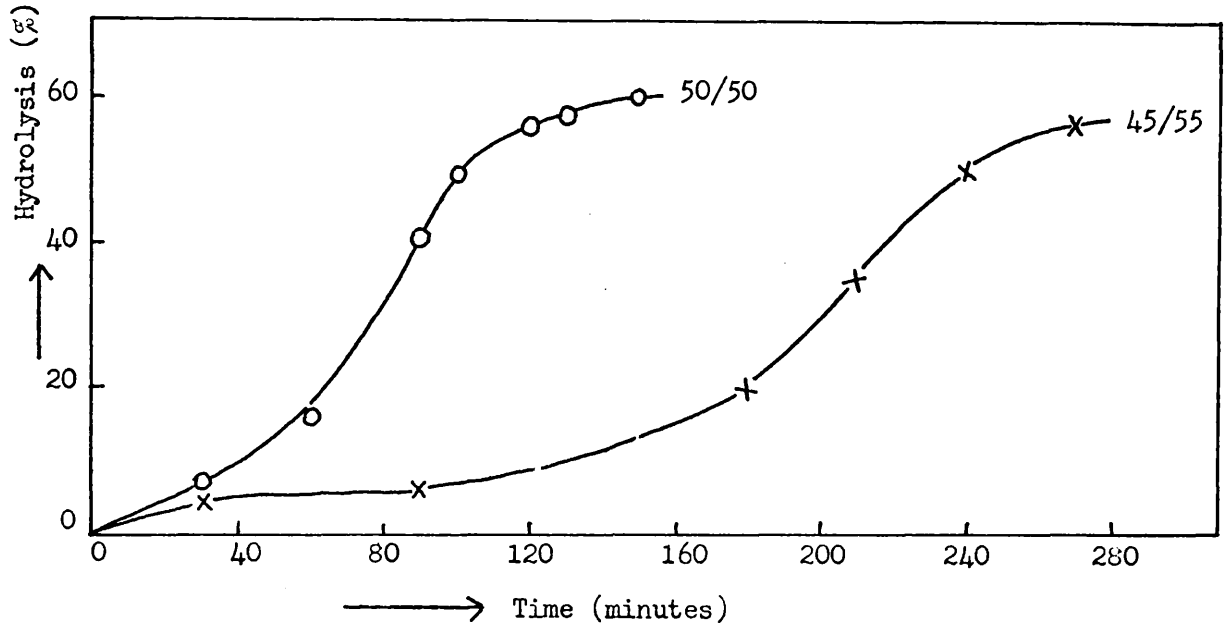
It is of interest that Arranz and Ashraf [78] have observed that in acetone/H_2O, $^{70}/_{30}$ the initial rate of the reaction is independent of the NaOH/ester ratio. They suggest that the reaction is accelerated in partially hydrolysed material by the formation of a hydrogen bond between a hydroxyl group of a

Table 3.4.

Saponification of PV-OAc in Acetone/H_2O at temperature 25°C for various solvent mixtures.

(PV-OAc, 0·23M; NaOH, 0·3M)

Medium	Time (Min)	% Hydrolysis	Medium	Time (Min)	% Hydrolysis
Acetone/H_2O, $^{50}/_{50}$	30	6·672	Acetone/H_2O, $^{55}/_{45}$	2	4·96
"	60	15·95	"	10	12·93
"	90	40·575	"	20	16·97
			"	30	25·24
"	100	49·26	"	40	39·77
"	120	55·714	"	50	51·07
"	140	58·74	"	60	56·123
			"	70	58·14
"	150	59·34	"	80	59·15
Acetone/H_2O, $^{45}/_{55}$	30	4·73	Acetone/H_2O, $^{65}/_{35}$	10	38·16
"	90	5·866	"	20	56·32
"	180	19·79	"	25	58·14
"	210	34·93	"	30	59·75
"	240	50·27	Acetone/H_2O, $^{70}/_{30}$	2	22·21
"	270	56·93	"	10	57·123
			"	15	60·04
"	325	59·76			



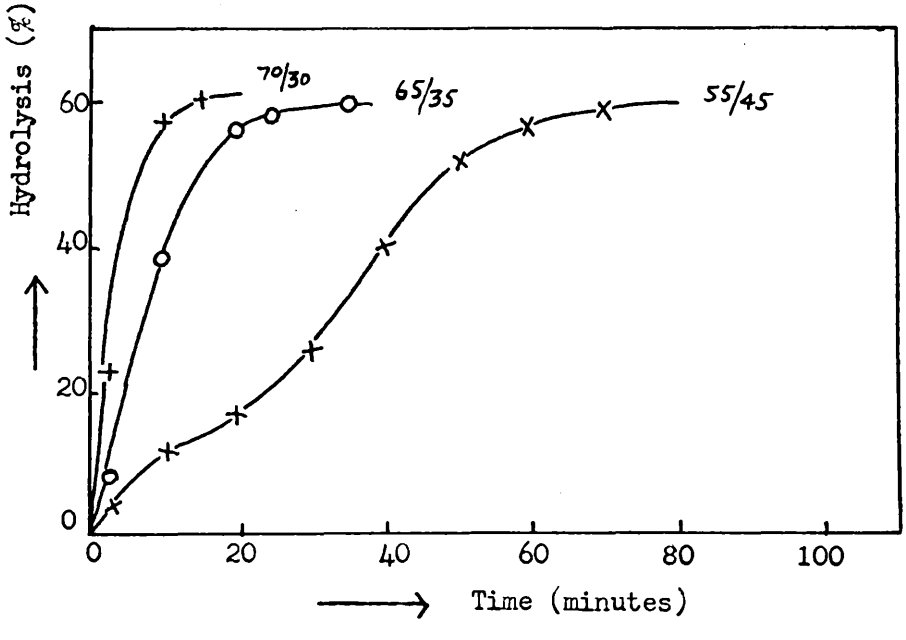


Fig. 3:6 PV-OAc hydrolysis yield as a function of time for various solvent mixtures. (Acetone/H_2O).

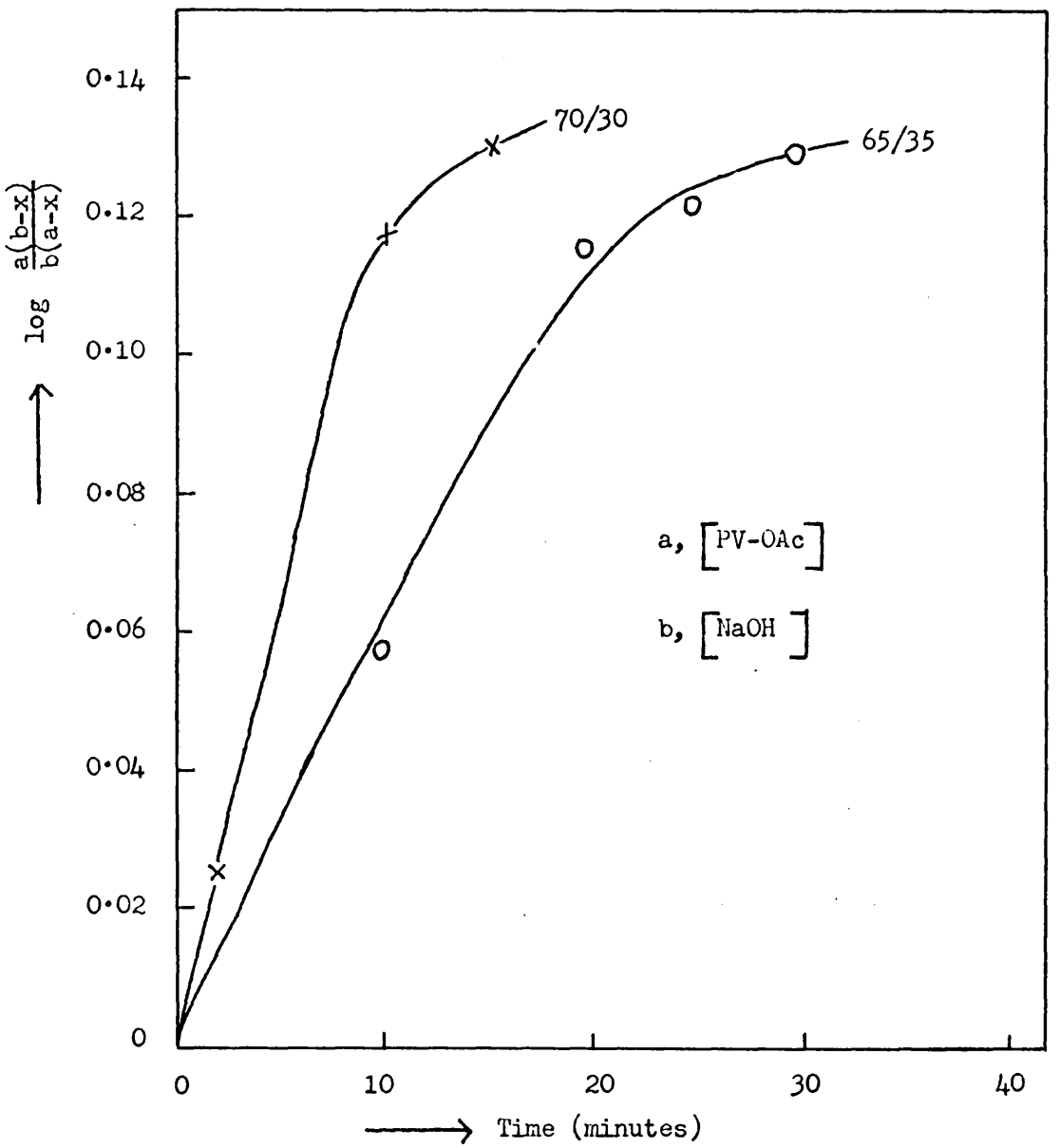


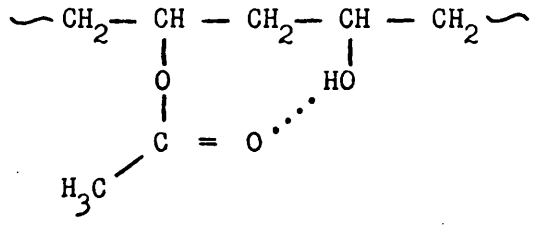
Fig. 3:7 Second order plots of saponification of PV-OAc in Acetone/H_2O solvent mixtures at temperature 25°C.

Table 3.5.

Rate Constants k_o of Saponification and Alcoholysis of PV-OAc.

Temperature (°C)	Catalyst	Solvent	k_o (l/mole min)
25	NaOH (0·3M)	Acetone/H_2O, $^{70}/_{30}$	46·06 x 10^{-2}
"	"	Acetone/H_2O, $^{65}/_{35}$	19·74 x 10^{-2}
"	"	Ethanol/H_2O, $^{70}/_{30}$	13·16 x 10^{-2}
"	"	Ethanol/H_2O, $^{60}/_{40}$	16·45 x 10^{-2}
"	KOH (0·3M)	Acetone/H_2O, $^{70}/_{30}$	49·39 x 10^{-2}
"	"	Acetone/H_2O, $^{65}/_{35}$	44·45 x 10^{-2}

hydrolysed unit and the carbonyl group of an adjacent ester unit. The presence of such hydrogen bond has been confirmed by



Nagai et. al. [15] using I.R. spectroscopy.

(b) Alcoholysis in Ethanol/H_2O. The intrinsic data for alcoholysis in ethanol/H_2O, $^{70}/30$ and $^{60}/40$ are presented in Table 3.6, and illustrated in Fig. 3:8. For these solvent composition the polymer was soluble. Second order plots were obtained as in Fig. 3:9 and the rate constants reported in Table 3.5 are obviously dependent upon the composition of the solvent. In contrast to the methanol/H_2O and acetone/H_2O systems, however, the rate of the reaction increases rather than decreases with increase in the proportion of water in the solvent in spite of the fact that one would still expect, in the ethanol/H_2O system, mixtures richer in water to be less good solvents. Thus some other effect must be overcoming the chain coiling factor in influencing the rate of reaction. This may be represented in terms of the generally accepted alcoholysis mechanism [79] shown in Fig. 3:10. In this mechanism the last step in the formation of a hydroxyl group involves the release of the ion active in the first step of the process. If the chain is expanded, this ion may rapidly diffuse in the solvent, but if the chain is more coiled, it is trapped in the coil and may readily attack an adjacent carbonyl group. Thus the acceleration in the rate may be visualised as a progressive trapping of the catalyst ion by the coiled macromolecules.

Table 3.6.

Alcoholysis of PV-OAc in Ethanol/H_2O at temperature 25°C

Medium	Time (Min)	% Alcoholysis
Ethanol/H_2O, $^{70}/_{30}$	2	10·9
"	7	32·1
"	12	39·17
"	24	46·23
"	41	53·1
"	55	56·33
"	77	58·95
"	84	59·56
Ethanol/H_2O, $^{60}/_{40}$	6	29·88
"	12	37·55
"	24	48·4
"	37	54·7
"	43	57·0
"	61	59·15
"	67	59·56

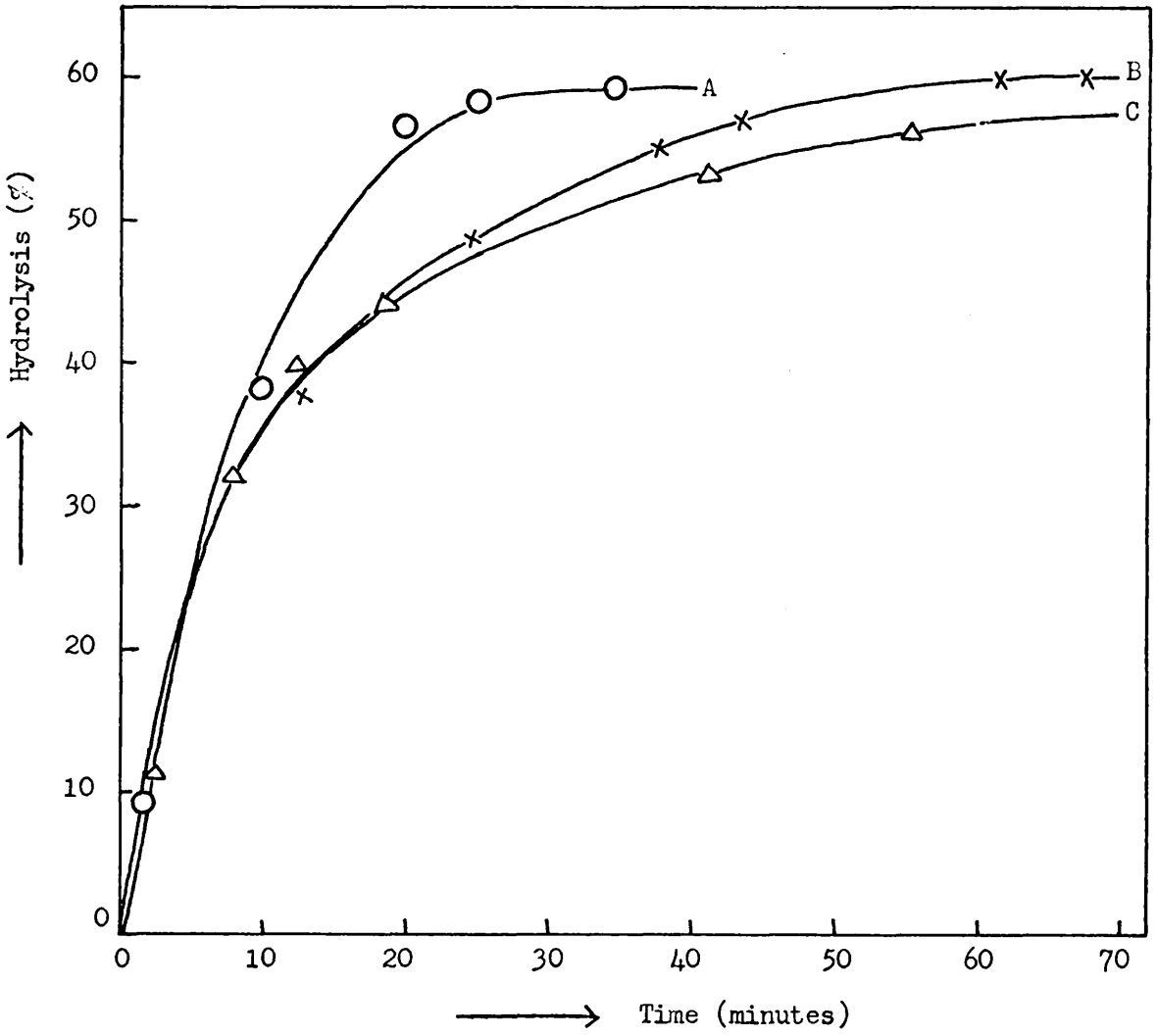


Fig. 3:8 PV-OAc Hydrolysis as a function of time at 25°C

A = acetone/H_2O, $^{65}/35$

B = ethanol/H_2O, $^{60}/40$, $^{65}/35$

C = ethanol/H_2O, $^{70}/30$.

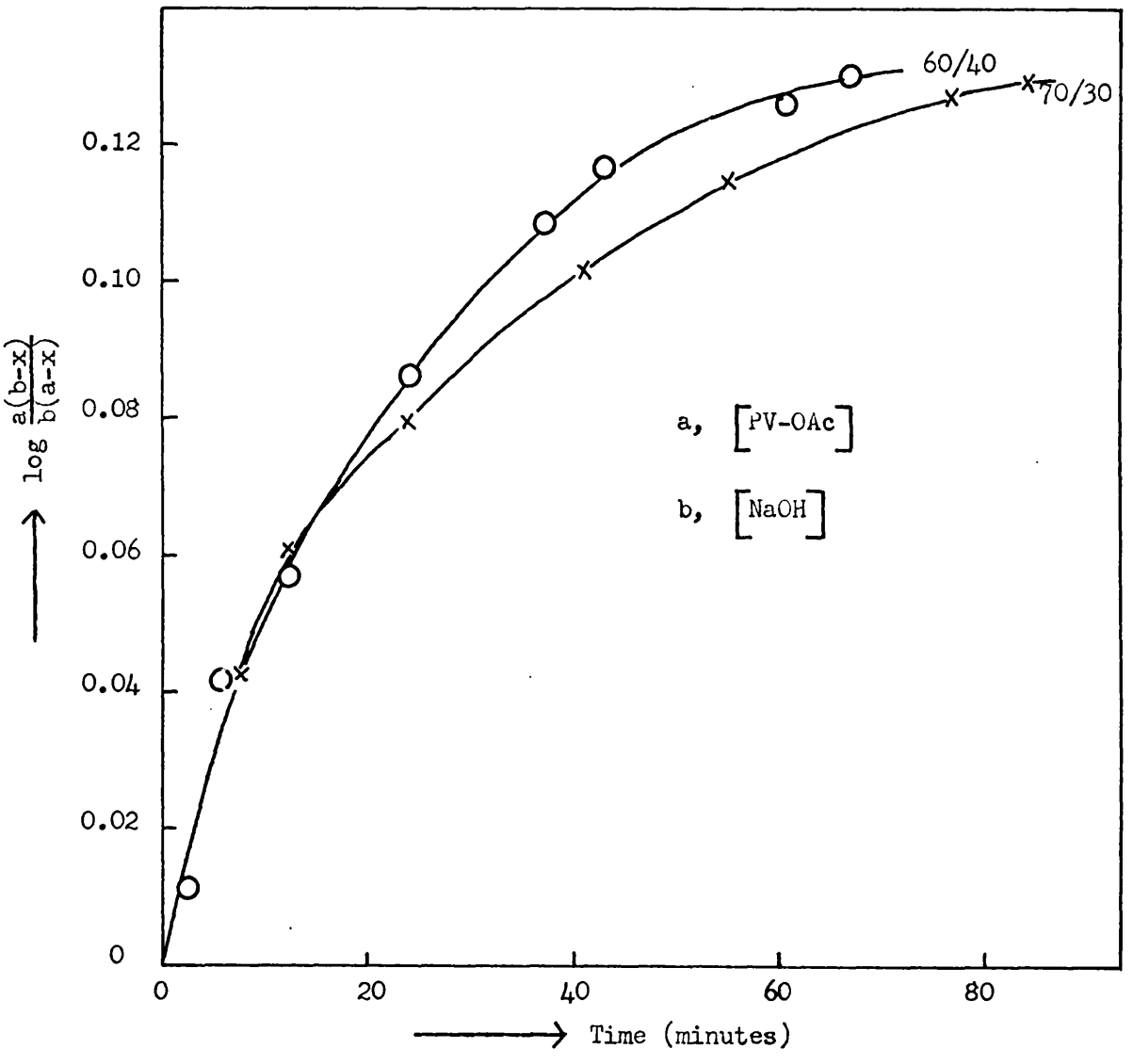
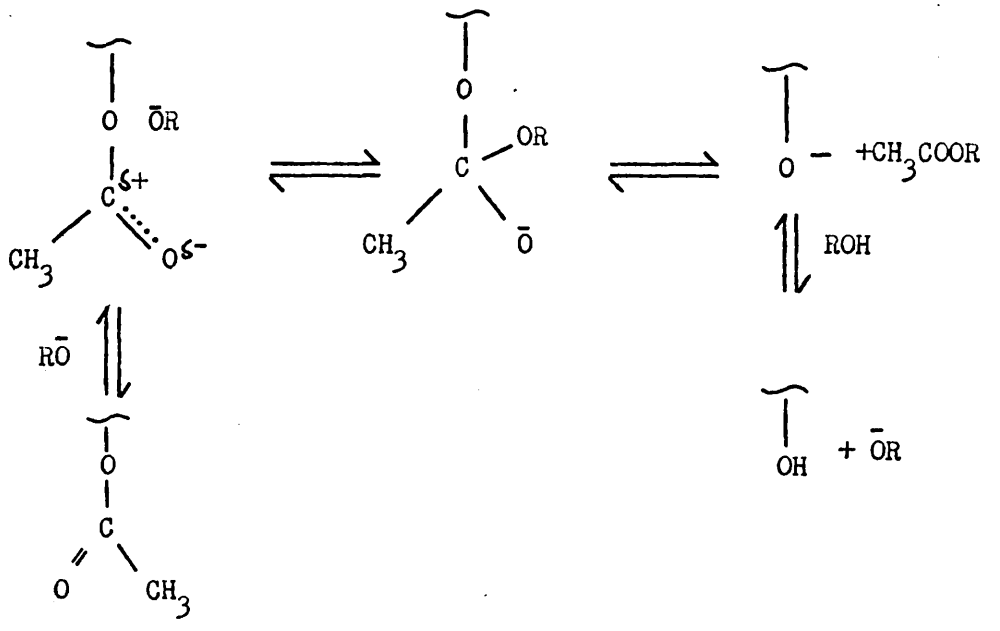


Fig. 3:9 Second order plots of alcoholysis of PV-OAc in ethanol/H_2O at 25°C.



R = alkyl group.

Fig. 3:10 Alkaline alcoholysis mechanism.

C. Viscosity Measurements of PV-OAc Solutions.

It has been suggested in a previous section of this chapter that the state of coiling of the PV-OAc molecules plays an important role in determining the main characteristics of their hydrolysis or alcoholysis. The state of coiling of polymer molecules in a solution is qualitatively related to the intrinsic viscosity of the solution. In general, the better the solvent, the less coiled are the molecules and the higher is the intrinsic viscosity of the solution. Thus it is relevant to make viscosity measurements on the solutions in which the reactions have been studied.

(a) Viscosity Measurement in Acetone/H_2O. Plots of η_{sp}/c against polymer concentration for the polymer (M.W, 58,800) used in the degradation and another of higher molecular weight are reproduced

in Fig. 3:11. The intrinsic viscosities, $[\eta] = \eta_{sp}/c$ at zero concentration derived from these plots are presented in Table 3.7. The constants K and α calculated using the Mark-Houwink equation,

$$[\eta] = KM^{\alpha} \text{ or } \log[\eta] = \log K + \alpha \log M$$

are given in Table 3.8. The value of α is a measure of the extent of coiling of the long chain molecule when the chain is tightly coiled into a sphere, the value of α approaches zero. As the chain becomes more highly extended the value increases to unity [80]. The value of K changes in different solvents in a way opposite to the intrinsic viscosity [81]. Thus it is clear from the α values in Table 3.8 that the PV-OAc molecules are more tightly coiled the greater the proportion of water in the acetone/H_2O solvent mixture.

(b) Viscosity Measurement in Ethanol/H_2O. Fig. 3:12 and Table 3.7 show the plots η_{sp}/c against polymer concentration and the intrinsic viscosity data respectively. The higher intrinsic viscosity of the polymer in ethanol/H_2O, $^{70}/_{30}$ than in ethanol/H_2O, $^{60}/_{40}$ indicates that the former solvent is better for the polymer than the latter solvent in spite of the fact that the rate of the reaction is higher in the latter as discussed in section B.(b) of the present chapter.

(c) Viscosity of Partially Saponified PV-OAc in Acetone/H_2O, $^{70}/_{30}$. Table 3.7 shows that the intrinsic viscosity of a partially saponified PV-OAc is higher than that of the parent PV-OAc. This means that the molecules of the partially saponified polymer are more highly extended probably due to the increase in the hydroxyl content which increases the polymer-solvent interaction. Although viscosity measurements were not carried out in solvents in which the polymer was insoluble, for obvious reasons, this can account

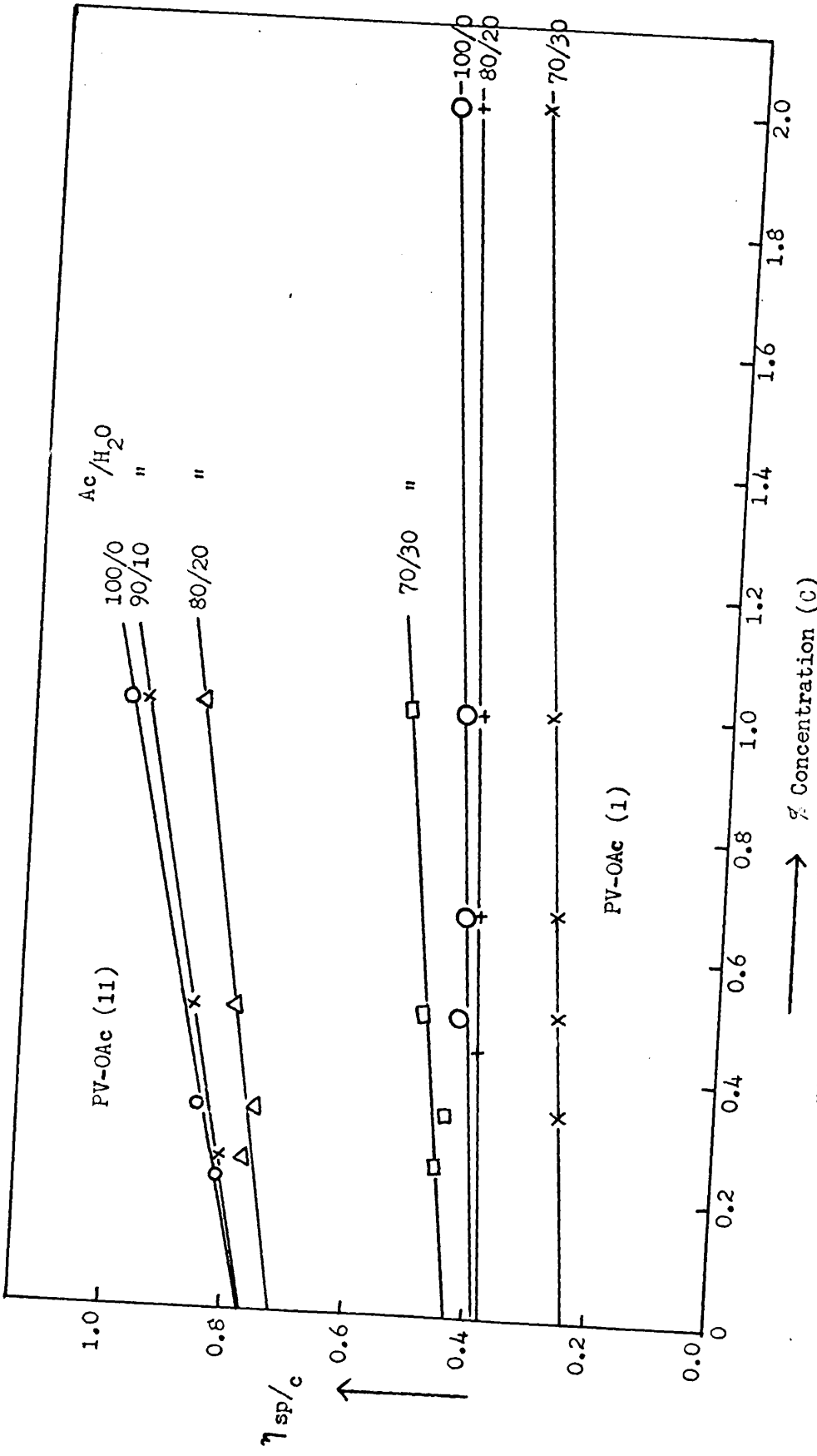


Fig. 3:11 Plots $\eta_{sp/c}$ versus polymer concentration.

Table 3.7.

Intrinsic Viscosity Data for PV-OAc at 25°C.

Solvent Composition	Intrinsic Viscosity dl/g	
	PV-OAc I M.W. 58,800	PV-OAc II M.W. 169,400
Acetone/H_2O, $^{100}/_{0}$	0·38	0·77
$^{90}/_{10}$	0·38	0·77
$^{80}/_{20}$	0·375	0·72
$^{70}/_{30}$	0·24	0·43
$^{70}/_{30}$	0·44*	
Ethanol/H_2O, $^{70}/_{30}$	0·29	
$^{60}/_{40}$	0·235	

* Intrinsic viscosity of partially saponified PV-OAc (>20%) prepared in acetone/H_2O, $^{70}/_{30}$.

Table 3.8.

Mark-Houwink Constants K and α at 25°C.

Solvent Composition (Acetone/H_2O)	K x 10^{-3}	α
100/0	21·88	0·7
90/10	21·88	0·7
80/20	41·96	0·625
70/30	50·12	0·533

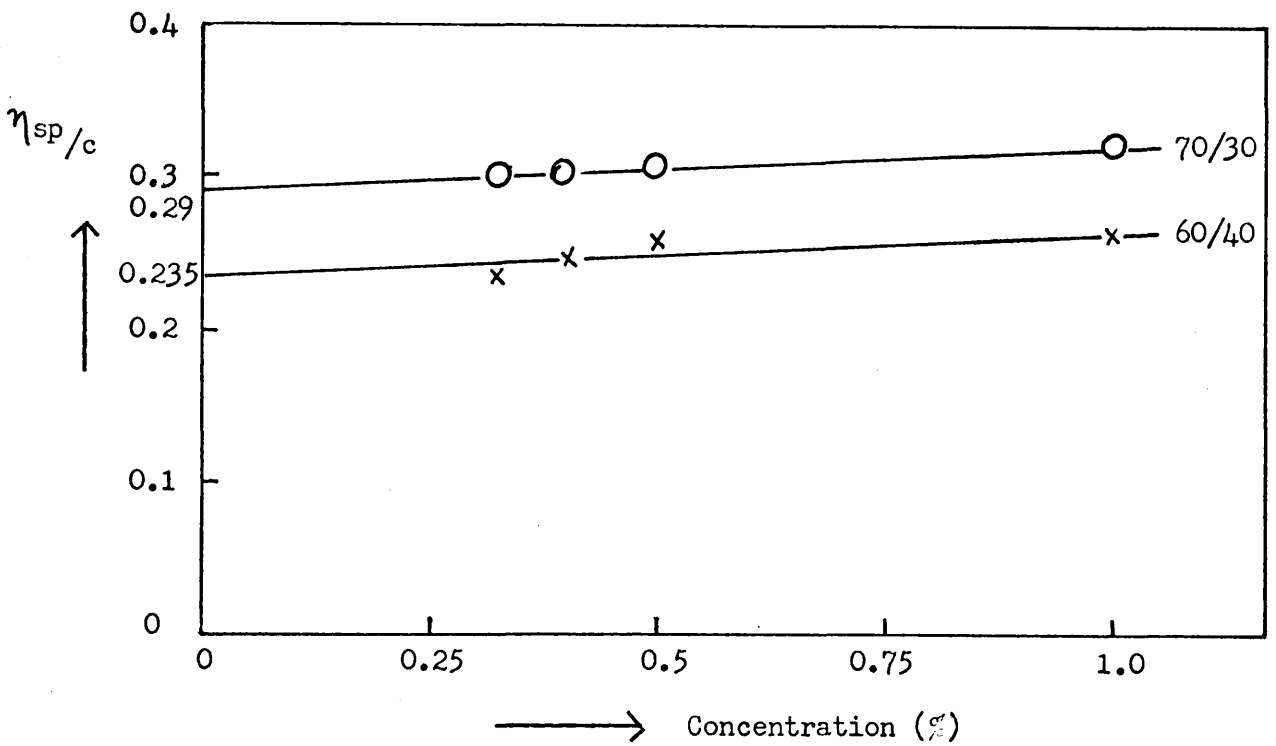


Fig. 3:12 Intrinsic viscosity of PV-OAc in Ethanol/H_2O at 25°C

$[\eta]$ —o— 0.29 dl/g

—x— 0.235 dl/g

for the autocatalytic properties exhibited by insoluble polymer.

D. Effect of the Nature of Catalyst on the Rate of Reaction.

Table 3.5 and Fig. 3:13 compare the relative catalytic activities of KOH and NaOH. KOH is a more effective catalyst and this may be associated with the fact that it is the stronger base, its activity coefficient being 0.742 compared with 0.708 for NaOH. Table 3.5 shows the second order rate constant values. There is a small difference in the rate constant values in acetone/H_2O, $^{70}/_{30}$, but the difference is more marked in acetone/H_2O, $^{65}/_{35}$. This could be due to the fact that dissociation of both bases in acetone/H_2O, $^{65}/_{35}$ is greater than in acetone/H_2O, $^{70}/_{30}$, the former being a more polar solvent than the latter.

3. Summary.

(i) The hydrolysis of PV-OAc in acetone/H_2O, methanol/H_2O and ethanol/H_2O have been studied using NaOH and KOH as catalysts.

(ii) The increase in the reaction rate mainly depends upon the extension of the polymer chains. The polymer chains become less coiled as the medium changes with temperature and the individual acetate groups are thus more liable to attack. The decrease in the rate in the later stages of the reaction is principally due to a decrease in the concentration of the reactants, but in the methanol/H_2O system the decrease in the rate may also be partly due to the increase in the methyl acetate concentration.

(iii) The initial rate is independent of the NaOH/ester ratio.

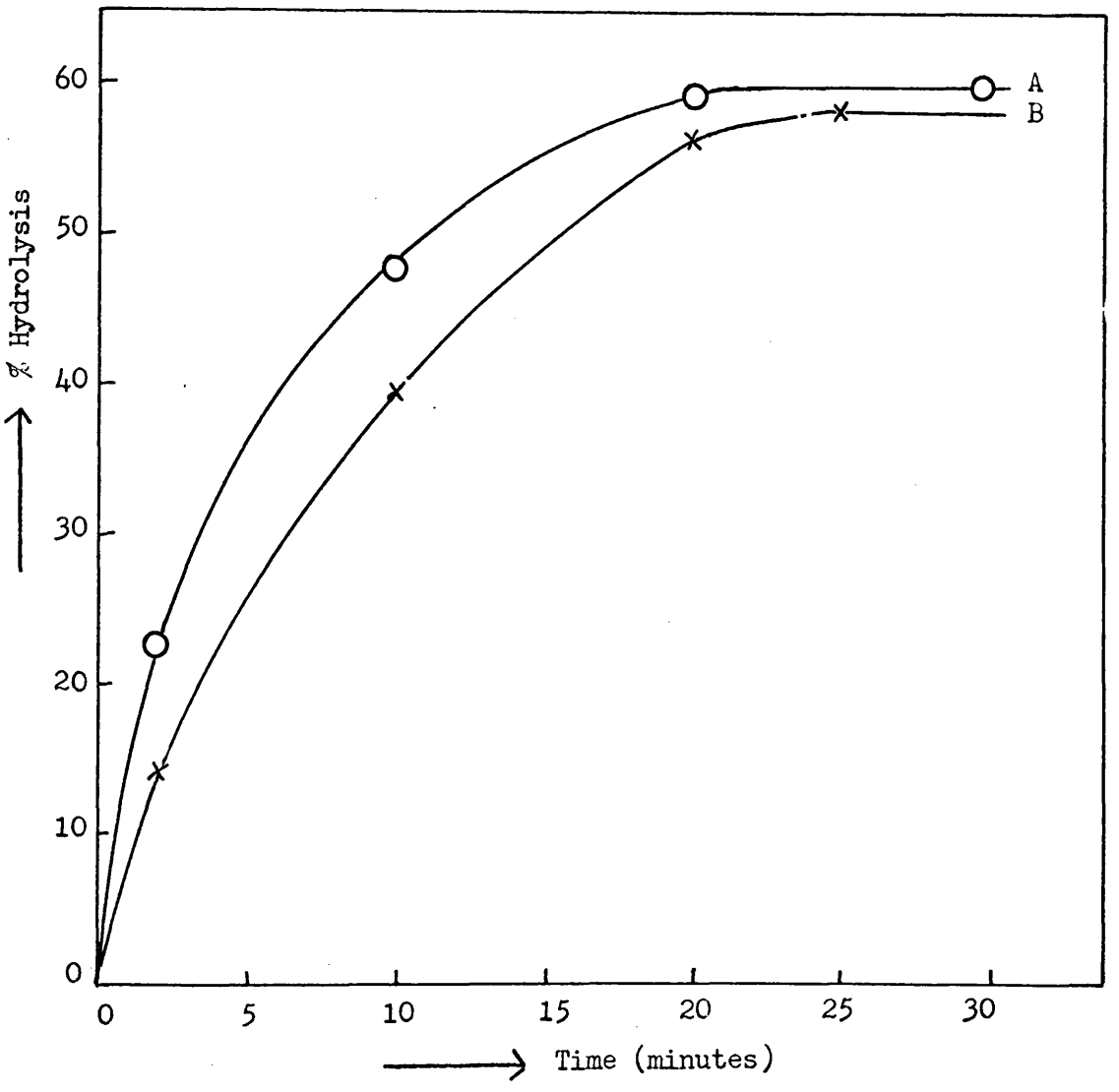


Fig. 3:13 Saponification of PV-OAc in acetone/H_2O, $^{65}/_{35}$ as a function of time in:

A — KOH (0·3M)

B — NaOH (0·3M).

(iv) In the acetone/H_2O system, the increase in the hydrolysis rate in the partially hydrolysed material may be due to the formation of a hydrogen bond between a hydroxyl group of a hydrolysed unit and the carboxyl group of an adjacent ester unit.

(v) The rate of a reaction responds to solvent composition. Attraction and repulsion effects of catalyst seem to be responsible for the change in the reaction rate.

(vi) Partially soluble polymers exhibit autocatalytic properties. In alcoholysis reactions, this may be due to the step-wise nature of the reaction.

(vii) In the ethanol/H_2O system, the rate is enhanced by a closer coiling of the macromolecules. It is suggested that the coiling favours the trapping of the catalyst ions.

(viii) The hydrolysis reaction follows second order kinetics in the initial stages of the reaction, where the effect of certain complicating factors responsible for the decrease in the reaction rate (mentioned above) is minimum.

(ix) Acetone is a better solvent for PV-OAc than its various mixtures with water.

(x) Potassium hydroxide is a more effective catalyst than NaOH for the hydrolysis of PV-OAc.

CHAPTER FOUR

THE THERMAL DEGRADATION OF POLY(VINYL ACETATE) AND COPOLYMERS OF VINYL ACETATE AND VINYL ALCOHOL

Poly(vinyl acetate) and poly(vinyl alcohol) exhibit similar degradation behaviours in that they both degrade by an elimination reaction which produces a residue containing conjugated double bonds and yields acetic acid and water respectively. Because of the similarity of their degradation reactions, copolymers of vinyl acetate and vinyl alcohol make an interesting system for investigation. The aim of the work described here is to study the thermal degradation of copolymers of a wide range of compositions; the thermal degradation of PV-OAc has also been studied in some detail.

1. The Thermal Degradation of Poly(Vinyl Acetate).

A. Introduction.

A description of previous work on the thermal degradation of PV-OAc has been given in Chapter One. Noma [25] in 1948 reported that scission occurs initially at the substituents. Sobue and his co-workers [26] reported in 1949 that the molecular weight of PV-OAc decreases on heating to temperatures between 280°C and 300°C. Grassie [27] described a detailed study on the subject. Based upon the analysis of the degradation products and residue, a non-radical chain reaction for the degradation mechanism was proposed. Madorsky [28] agreed with Grassie's findings. He also suggested that in some cases, abstraction of a hydrogen atom by an acetate free radical may take place intermolecularly

from other chains, thus resulting in cross-links.

Pavlinec and Kaloforov [29] have postulated that all the acetate groups have the same reactivity, leading to random loss of acetic acid along the polymer chain. Gardner and McNeill [30] and Zimmermann [31] studied the conjugated residue using ultra-violet spectroscopy and found between six and twelve conjugated double bond sequences in discoloured PV-OAc. Desreux [32] did not observe carbon dioxide and ketene as volatile degradation products as observed by Grassie [27] and Gardner and McNeill [30].

Therefore, although the overall reaction has been clearly formulated, the detailed mechanism of PV-OAc has not been fully elucidated.

B. Thermal Volatilisation Analysis.

Fig. 4:1 illustrates the TVA behaviour of PV-OAc. The large peak with a rate maximum around 355°C corresponds to elimination of acetic acid. However, in addition of acetic acid, products non-condensable at -75°C, -100°C and -196°C are clearly also evolved. The difference between the -75°C and -196°C traces, has been interpreted as being due to the presence of water, methane, carbon dioxide and ketene. Acetic acid is completely trapped at the three lowest temperatures, but at -45°C, it condenses and distills over to the liquid nitrogen trap at a steady rate, causing the -45°C trace to lie above the -75°C trace. This has been described as Limiting Rate behaviour [64].

The high temperature peak above 400°C results from products, a large proportion of which, are non-condensable at -196°C and which are formed by break up of the unsaturated polyene chains. Also occurring at these higher temperatures is the formation of aromatic rings from the conjugated olefinic chains by a Diels-Alder mechanism, either inter or

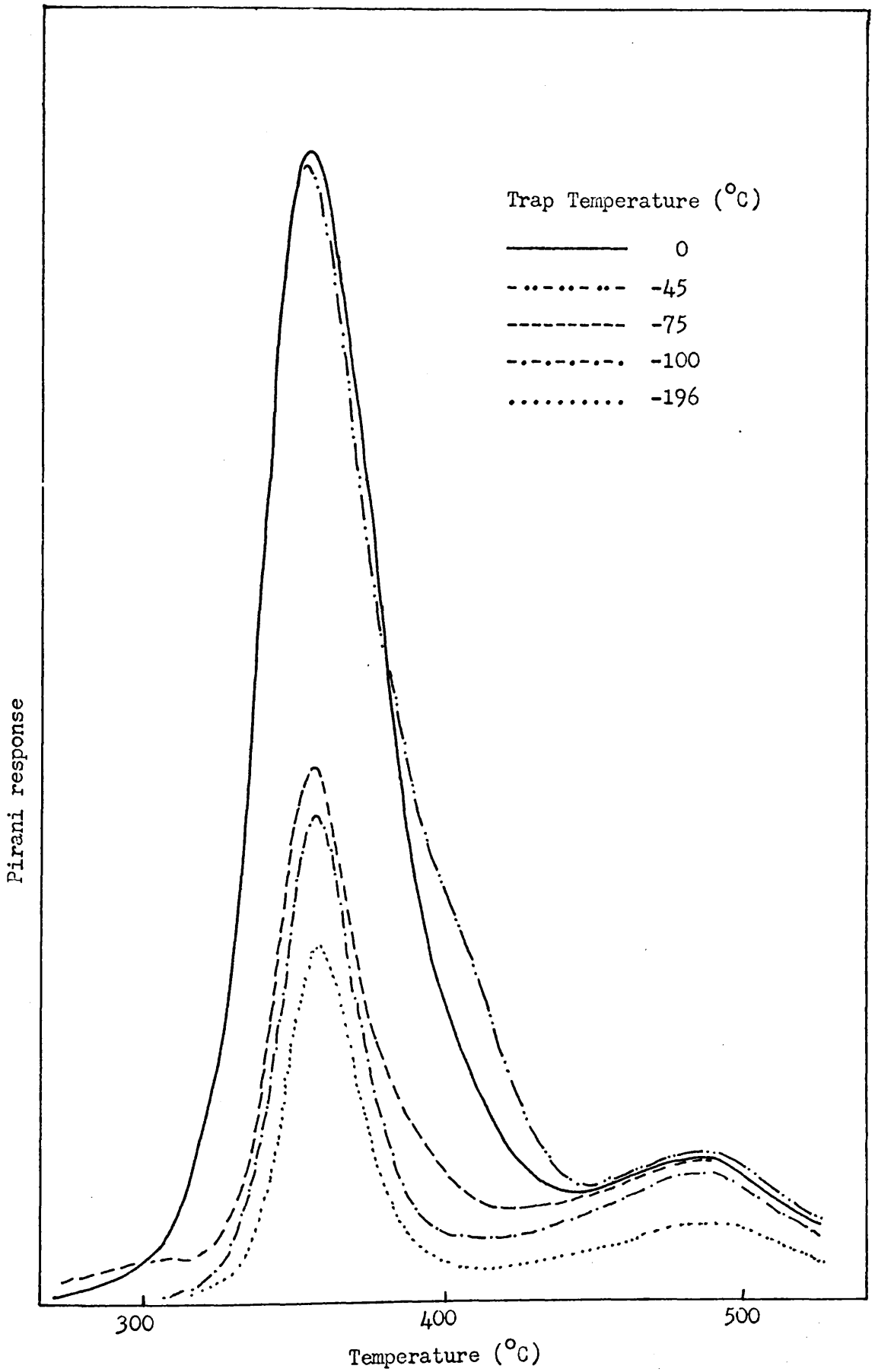
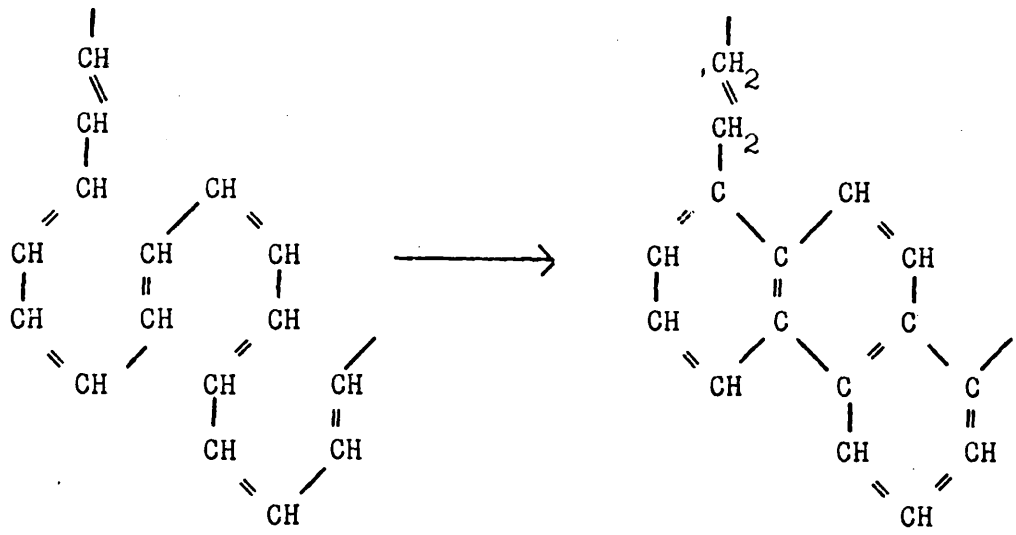


Fig. 4:1 TVA curve for PV-OAc.

intra molecularly. It is thought that this reaction does not proceed simply by elimination of hydrogen, but by hydrogen transfer to an adjacent unsaturated group [82,83].



(a) Product Identification. The degradation products from PV-OAc can be considered in fractions as follows,

(i) The involatile residue, comprising products involatile at 500°C under vacuum.

(ii) The "cold ring fraction" collected on the water cooled upper part of the TVA degradation tube which consists of products volatile at degradation temperatures but involatile at room temperature.

(iii) Volatile products condensable at -196°C.

(iv) Volatile products not condensable at -196°C.

Fraction (i).

The structure of the residue remaining at 500°C was examined by I.R. spectroscopy. In Fig. 4:2 (C), the broad spectrum indicates that all carbonyl groups have been eliminated from the polymer. The spectrum contains broad peaks above 3000 cm^{-1}, intense bands around 1600 cm^{-1} and

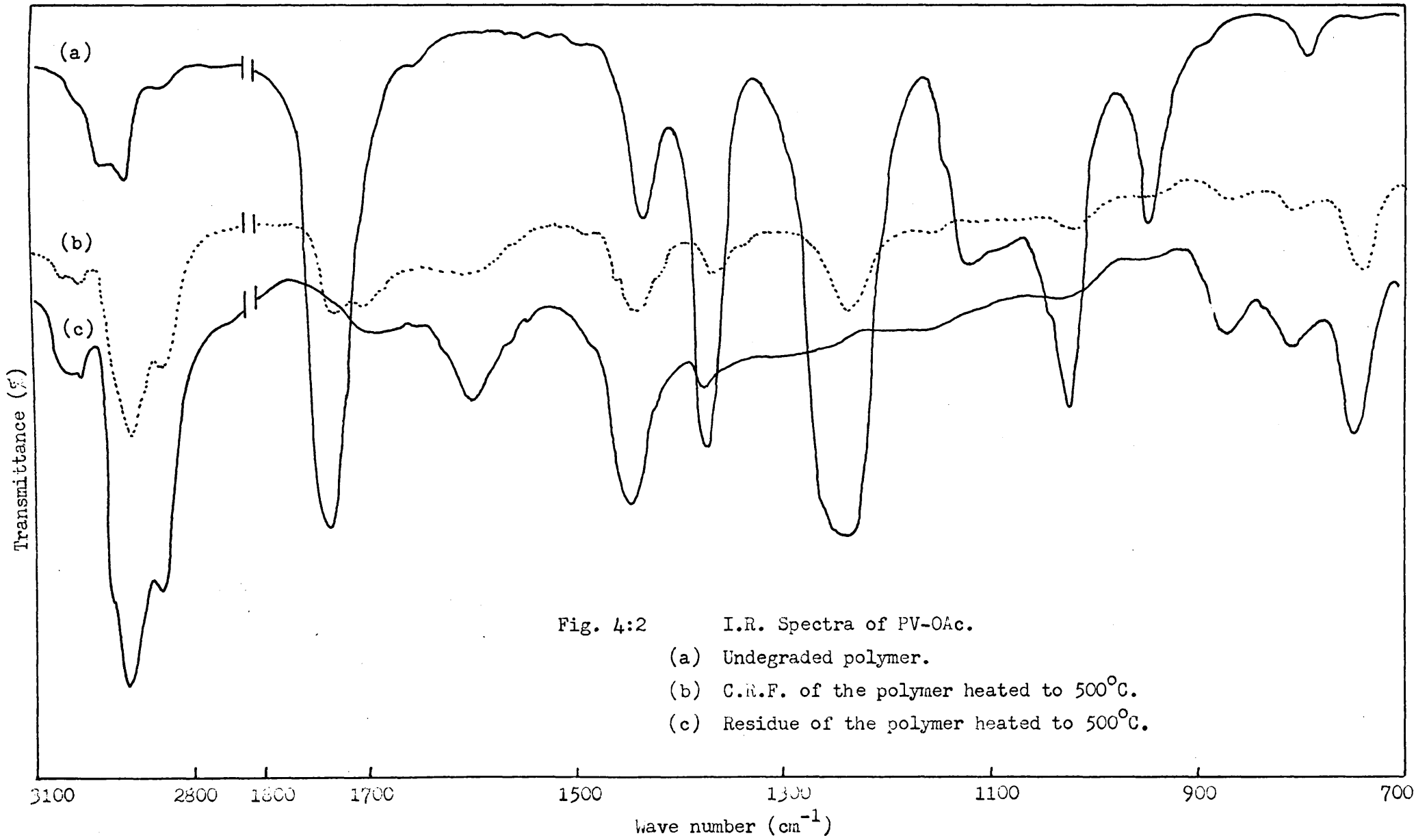


Fig. 4:2 I.R. Spectra of PV-OAc.

(a) Undegraded polymer.

(b) C.R.F. of the polymer heated to 500°C.

(c) Residue of the polymer heated to 500°C.

in the 800 - 900 cm^{-1} region associated with conjugation.

Fraction (ii).

Fig. 4:2 (b) shows the i.r. spectrum of the C.R.F. obtained from degradation to 500°C. This fraction is much greater than observed in TG employing a dynamic nitrogen atmosphere, principally due to the high vacuum conditions employed in TVA allowing a greater proportion of material involatile at ambient temperatures and pressures to be volatilised. The spectrum is almost identical to that of the parent copolymer except for a few broad peaks associated with conjugation similar to those found in the residue.

Fraction (iii).

Analysis of the condensable degradation products was carried out in the gas phase. Fig. 4:3 shows its i.r. spectrum. Tables 4.1 and 4.2 give the assignments of the peaks and degradation products respectively.

Fraction (iv).

The identity of the products which were not condensed at -196°C, shown also in Table 4.2 was established using the closed degradation system shown in Fig. 4:4. 100 - 150 mg of the polymer was placed in tube T, and the system was then evacuated through the stopcock C, taps A and B being open. All the taps were then closed. A cold trap at -196°C was placed around the cold finger D, and the sample was heated at 10°/min to 500°C, and then allowed to cool. Taps A and B were then opened and L was immersed in a liquid nitrogen bath. After 10 - 15 minutes A was closed, the cold trap was removed, the gas cell disconnected from the system, and a spectrum was taken. No attempt was made at quantitative measurement of the non-condensables.

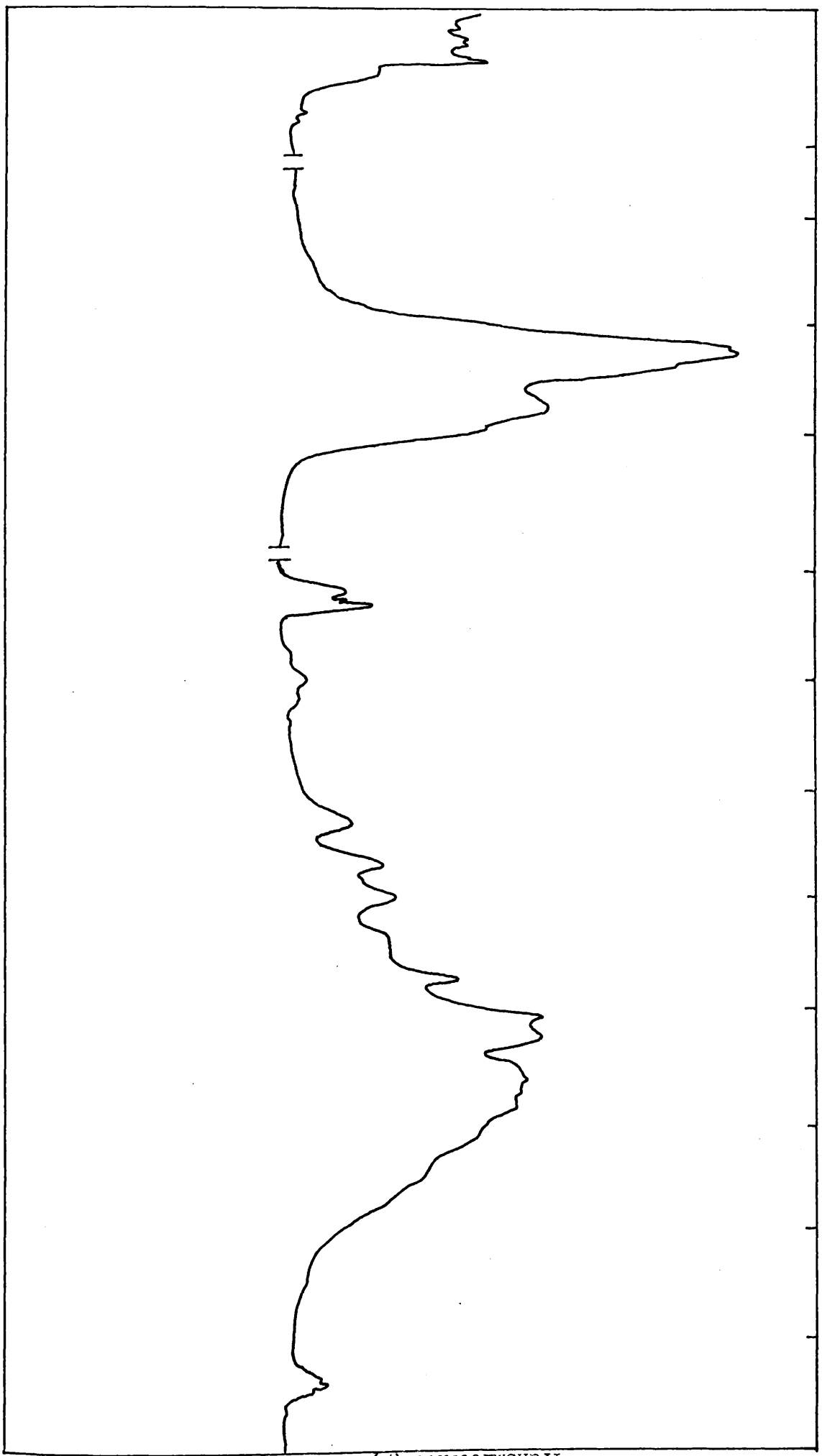


Fig. 4:3 I.R. Spectrum of the gaseous volatile products from PV-Ac.

Table 4.1.

Assignment of the I.R. Peaks of degradation products of PV-OAc.

Frequency cm^{-1}	Mode	Compound or group
3018	C - H stretching	Methane
2845-2965	C - H "	CH_3, CH_2, CH
2300-2340	C - O "	Carbon dioxide
2145	C - O "	Carbon monoxide
2140-2160		Ketene
1780	C = O "	Carbonyl
1730	C = O "	"
1295	C = O "	"
730	C - H out of plane Deformation	Acetylene
721	C - O bend	Carbon dioxide
675	C - H bend	Benzene
669	C - O "	Carbon dioxide

Table 4.2.

Volatile degradation products of PV-OAc.

Condensable at -196°C	non-Condensable at -196°C
CH_3COOH	CH_4 (Trace)
CO_2	CO (Trace)
Ketene	
H_2O	

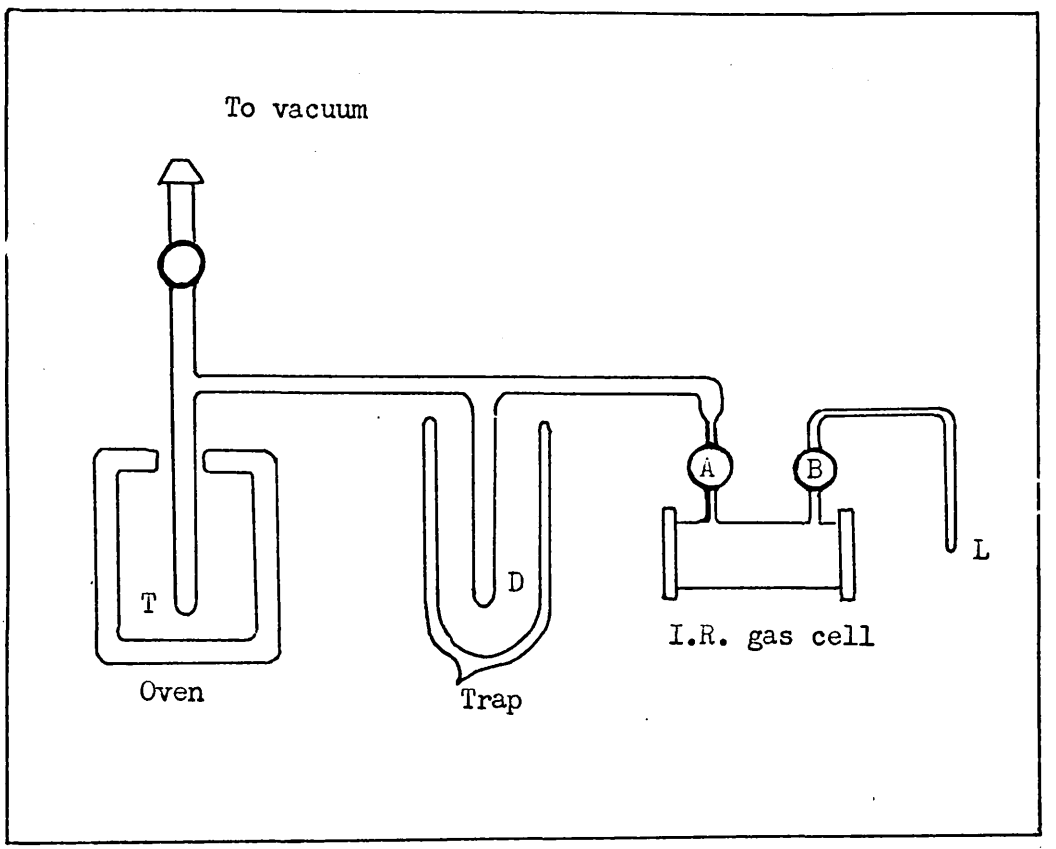


Fig. 4:4 Apparatus for infra-red analysis of volatile products (closed system). (A, B, C : stop cocks, D, L : cold fingers, T : sample tube).

C. Thermal Gravimetric Analysis.

TGA curves for PV-OAc degrading under nitrogen and in vacuum are given in Fig. 4:5. There are two distinct regions of weight loss leaving a small residue at 500°C. The first stage corresponds to the deacetylation of V-OAc units. The second stage of weight loss is due to decomposition of the ethylenic structures.

The percentage residue under nitrogen is higher than that obtained under vacuum. This difference is attributed to the short chain fragments which escape from the hot zone to the cold ring of the TVA tube under high vacuum conditions, while these fragments fail to do so under nitrogen. The thermal breakdown of the homopolymer starts at approximately the same temperature under vacuum and in nitrogen.

The loss in weight of the polymer which occurs during isothermal heating under nitrogen was investigated at 255, 265, 275 and 285°C. The rate of weight loss increases with the temperature (Fig. 4:6), slowing down as the reaction proceeds. Fig. 4:7 shows an Arrhenius plot of the initial rates from which a value of 35·6 k cals/mole may be calculated for the energy of activation. This compares well with the value of 37·9 $\pm$ 2·0 k cals/mole obtained by A. Jamieson [84].

D. Differential Thermal Analysis.

A DTA curve for PV-OAc is shown in Fig. 4:8. Deacetylation is represented by the endotherm stretching from 320°C to 385°C and the break up of the conjugated chains is reflected by an endotherm-exotherm system above 400°C. This confirms TVA observations.

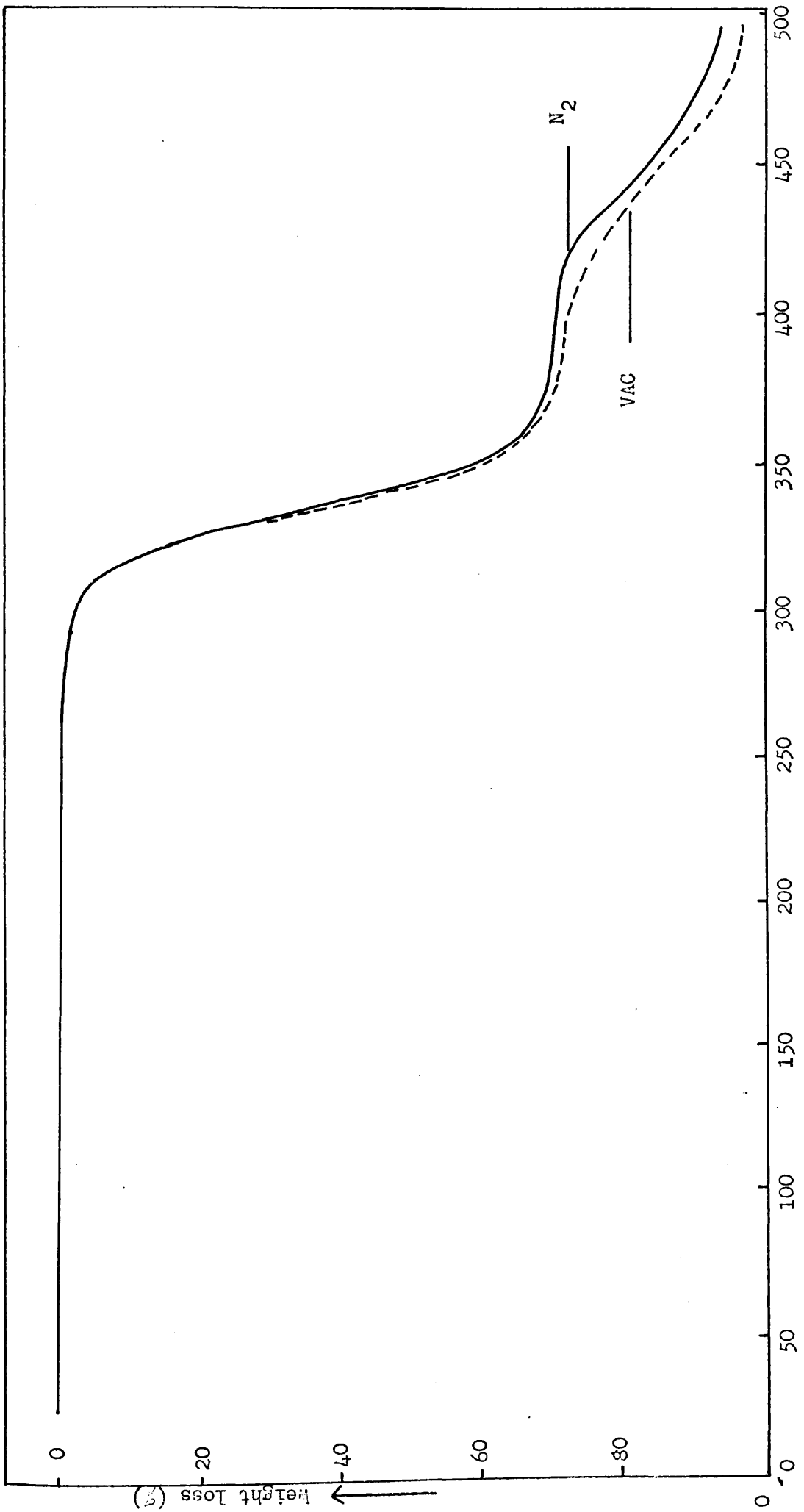


Fig. 4:5 TG curves for PV-OAc sample size 5 mg. Heating rate 10°C/min, under N_2 and vacuum.

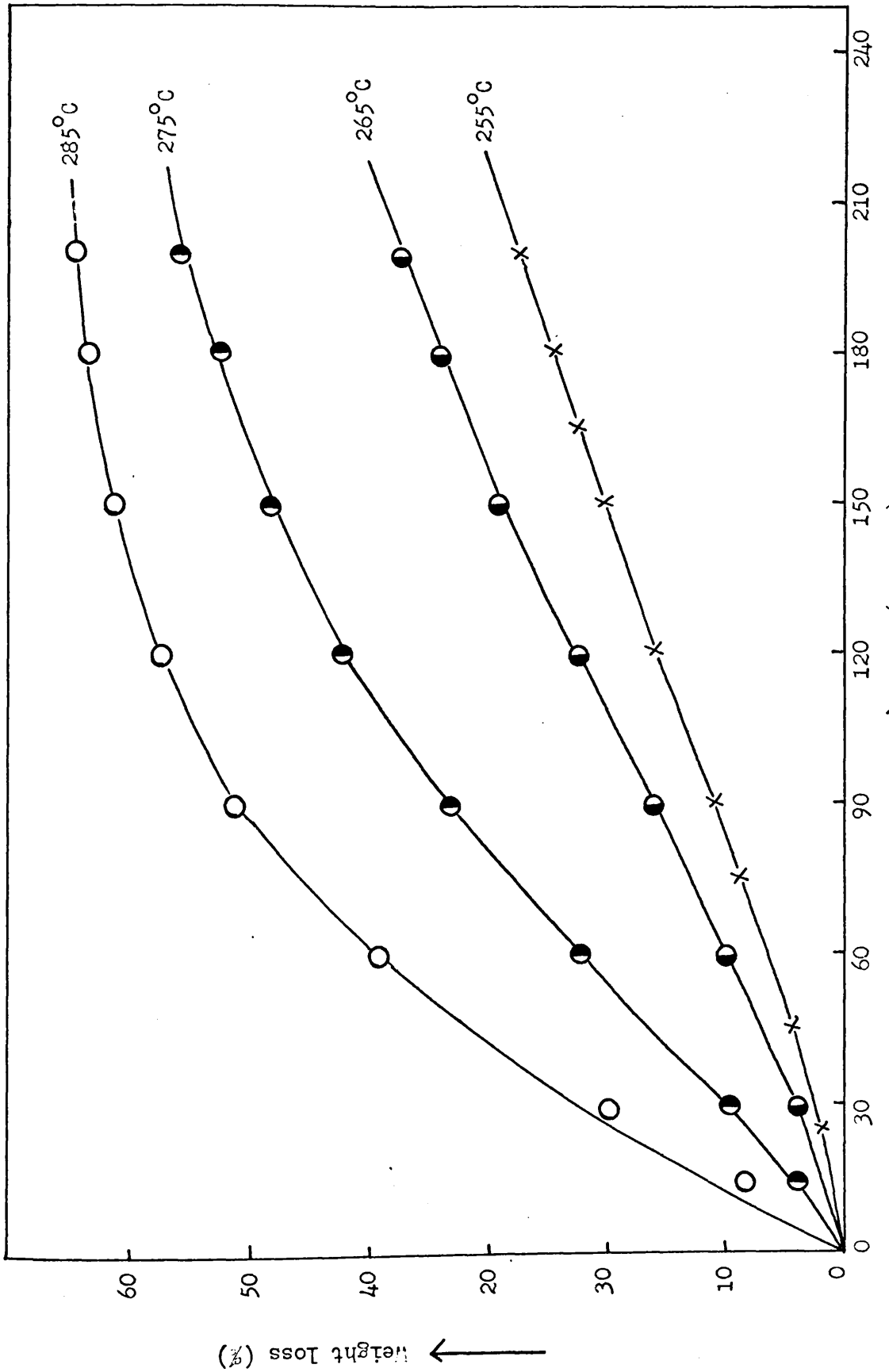


Fig. 4:6 Weight loss of PV-OAc as a function of time at various temperatures.

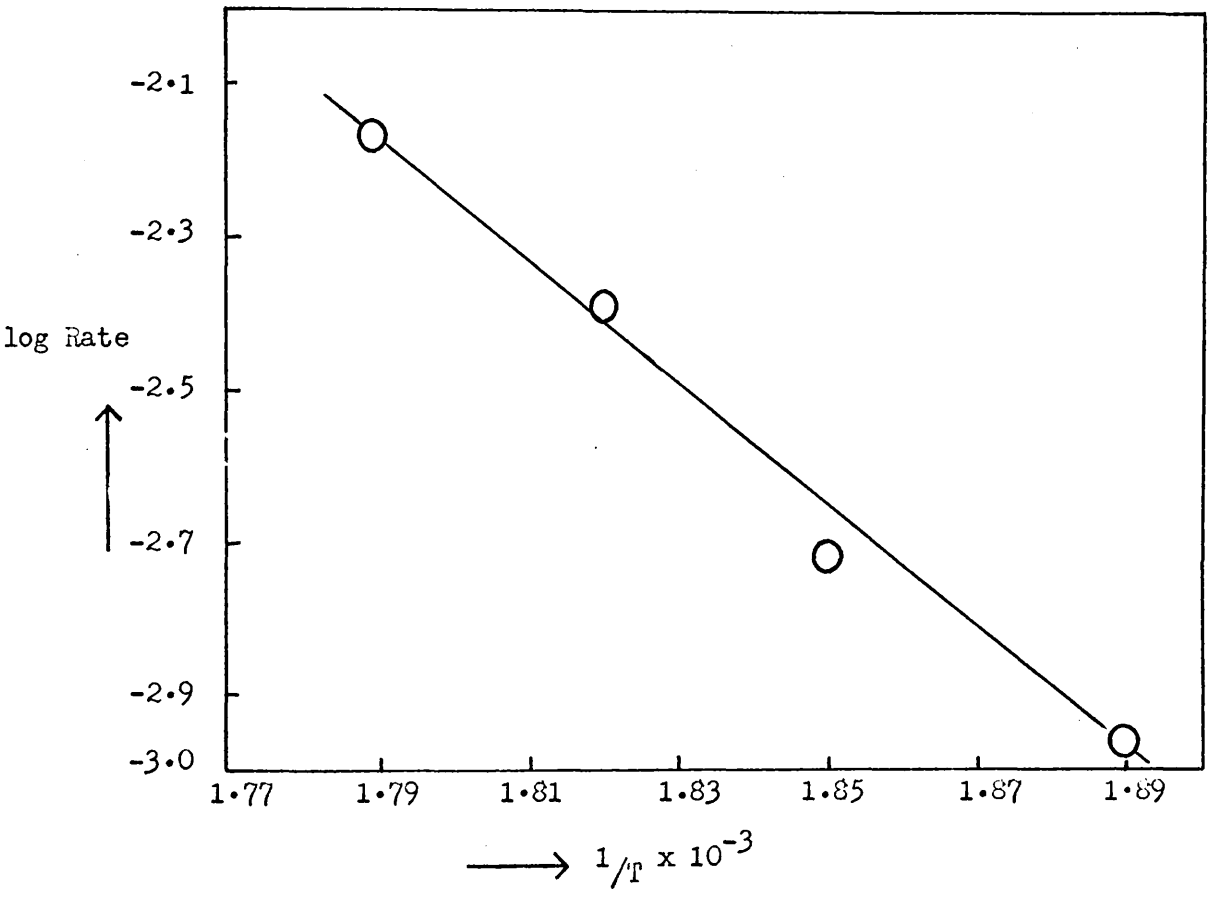


Fig. 4:7 Determination of the energy of activation for PV-OAc by plotting values of log Rate versus $^1/_T{}^oK$ (the Arrhenius plot).

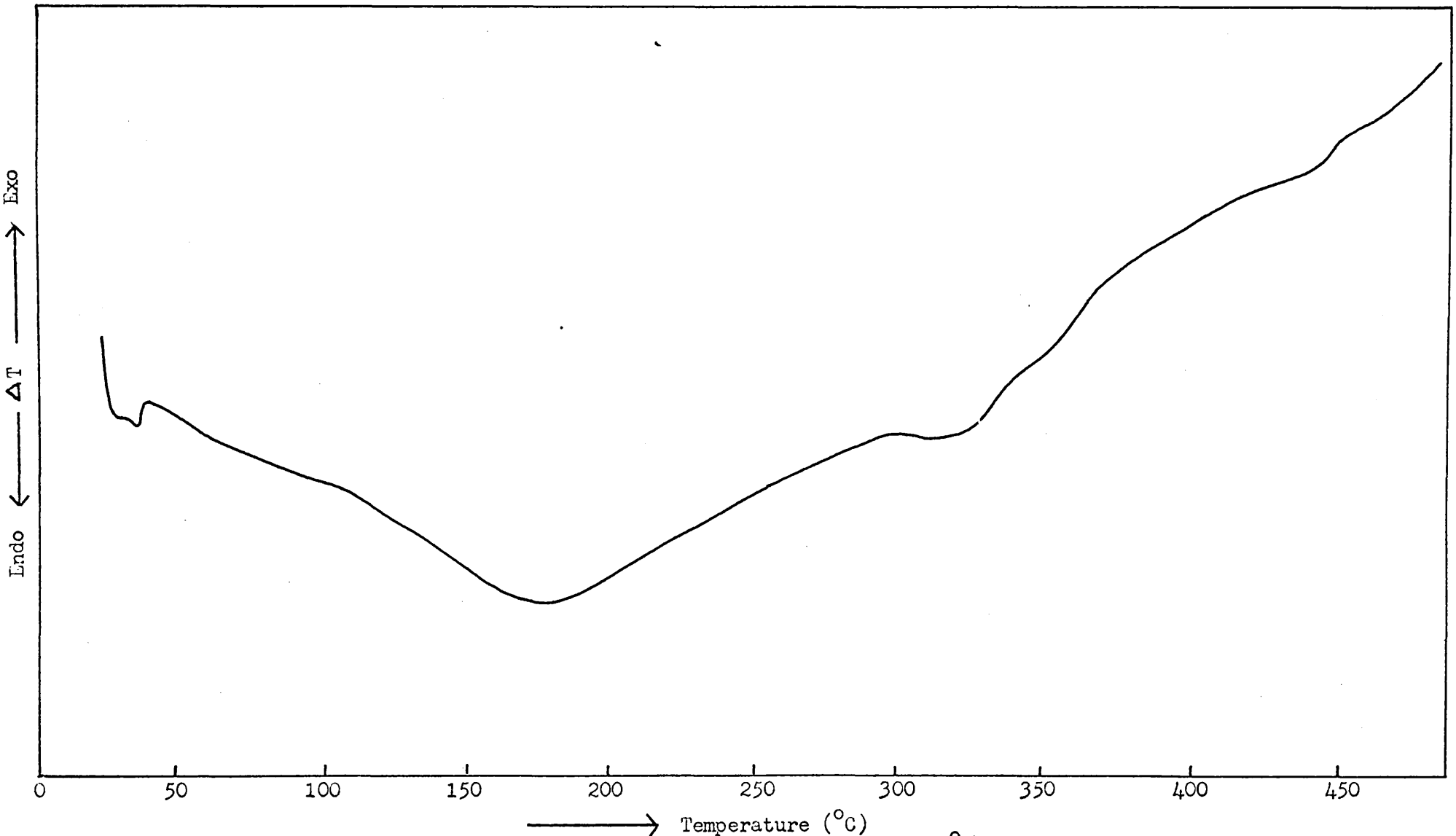


Fig. 4:8 DTA curve for PV-OAc, Dynamic nitrogen atmosphere, Heating rate 10°/min.

2. The Thermal Degradation of Copolymers of V-OAc and V-OH.

A. Introduction.

Nothing has been published about the mechanism of decomposition of V-OAc/V-OH copolymers. However, before describing our results, it is of interest to mention briefly investigations made by previous workers on some related copolymer systems.

The degradation of V-OAc/MMA copolymers has been briefly investigated by Daniel and Michel [85] and Gardner [86] who observed the production of acetic acid from the V-OAc units and MMA monomer from the MMA units. In V-OAc/AN copolymers, it was observed [87] that elimination of acetic acid was concurrent with the degradation reactions occurring in the AN sequences.

M.A.J. Mohammad [88], in a short study of V-OAc/S and V-OAc/E copolymers, suggested that degradation occurs initially at V-OAc sites, which he proposed were weak links in the copolymers. In V-OAc/E copolymers, Gardner [86] and A. Jamieson [84] noted that deacetylation of V-OAc units proceeds separately from and at lower temperatures than decomposition of the E units. In the light of these observations one might expect similar degradation behaviour in V-OAc/V-OH copolymers.

B. Thermal Volatilisation Analysis.

TVA traces for four V-OAc/V-OH copolymers prepared by saponification and containing 53·19%, 7·72%, 2·67% and 0·6% V-OAc are reproduced in Figs. 4:9, 4:10, 4:11 and 4:12 respectively.

The initial sharp peak of PV-OAc (Fig. 4:1) is shifted to higher temperature as the acetate content in the copolymer decreases indicating greater stability in the copolymer. As the proportion of V-OAc units in the copolymer is decreased the shape and relative positions of the five traces in the thermogram gradually lose the characteristics of the

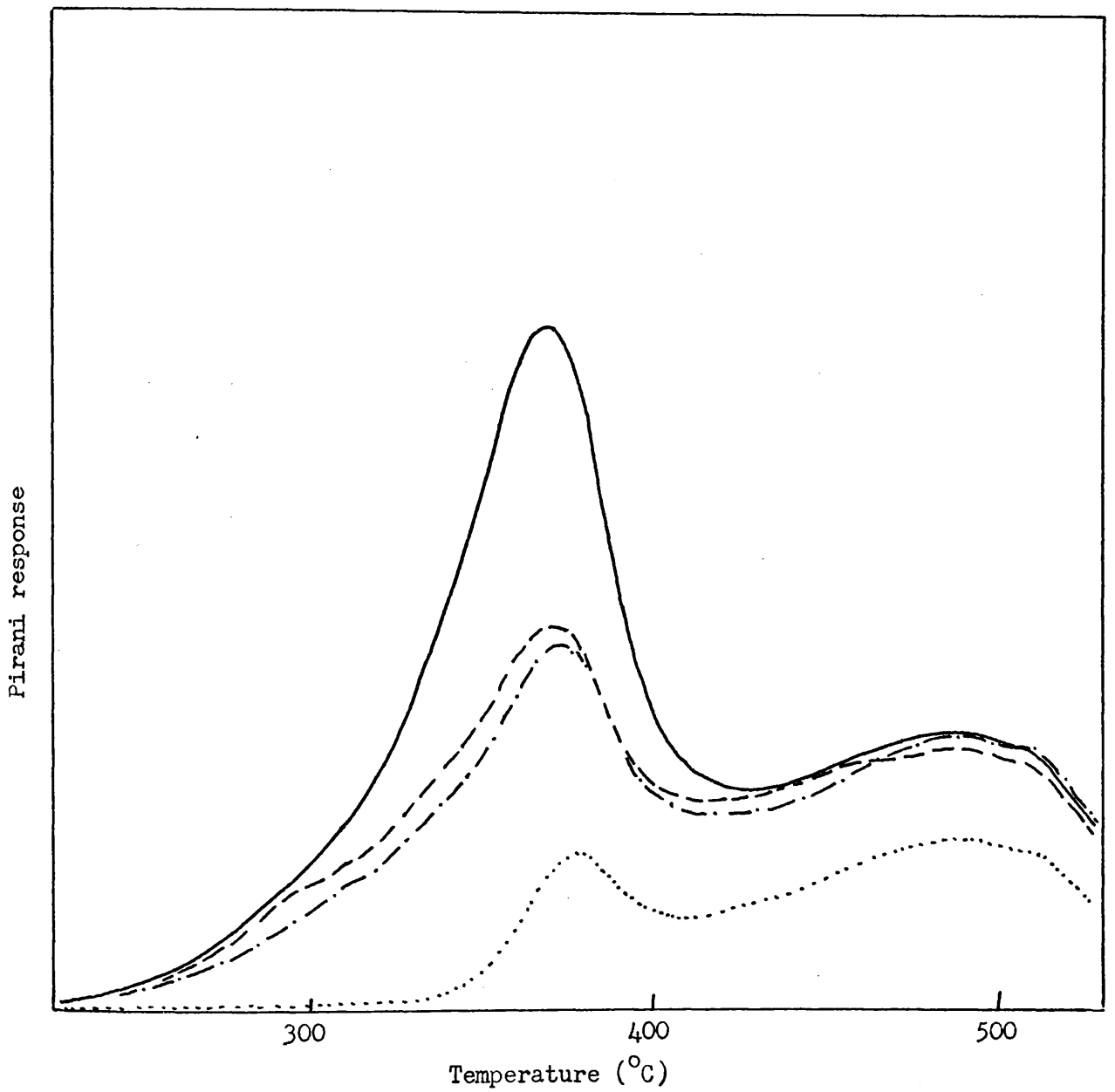


Fig. 4:9 TVA curve for 53·19% saponified copolymer.

Trap Temperature (°C)

———— 0, -45

– – – – – -75

–.–.–.–.– -100

..... -196°C

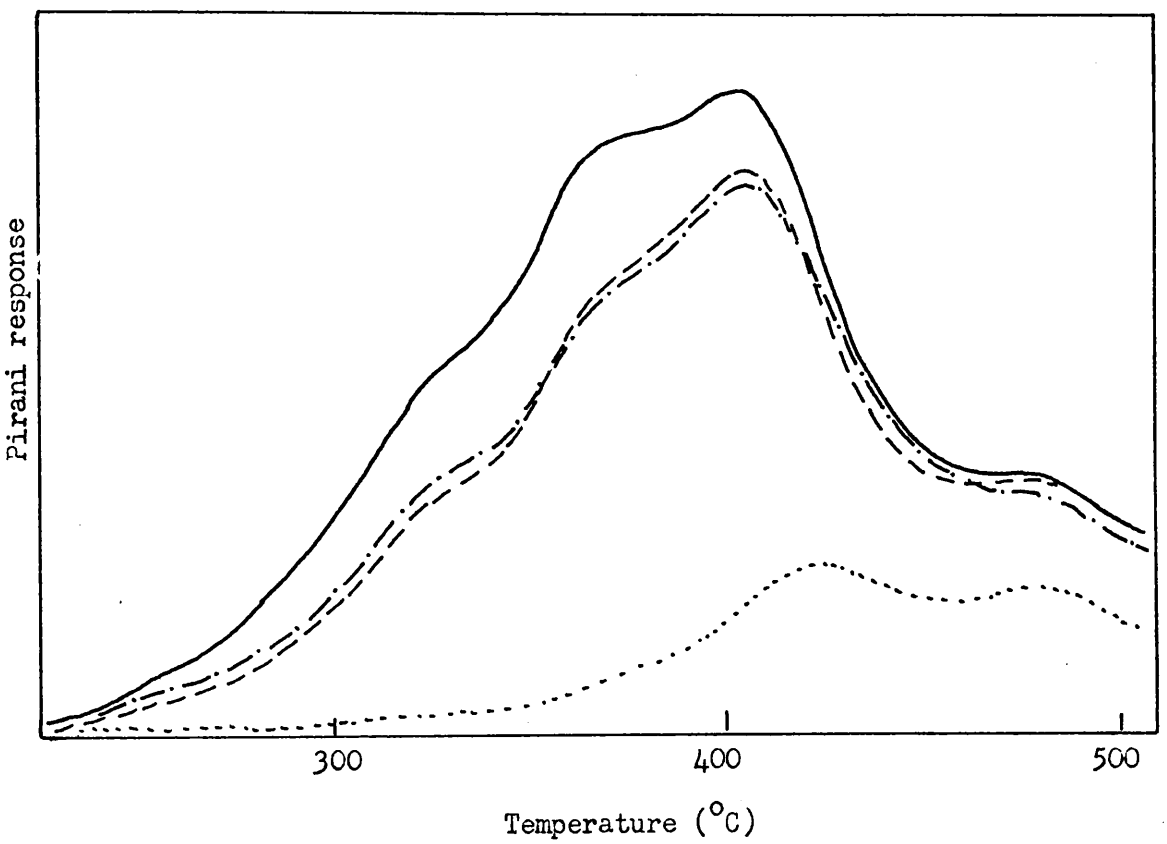


Fig. 4:10 TVA curve for 7·72% saponified copolymer.

Trap Temperature (°C)

———— 0, -45

– – – – – – -75

—·—·—·—·— -100

..... -196°C

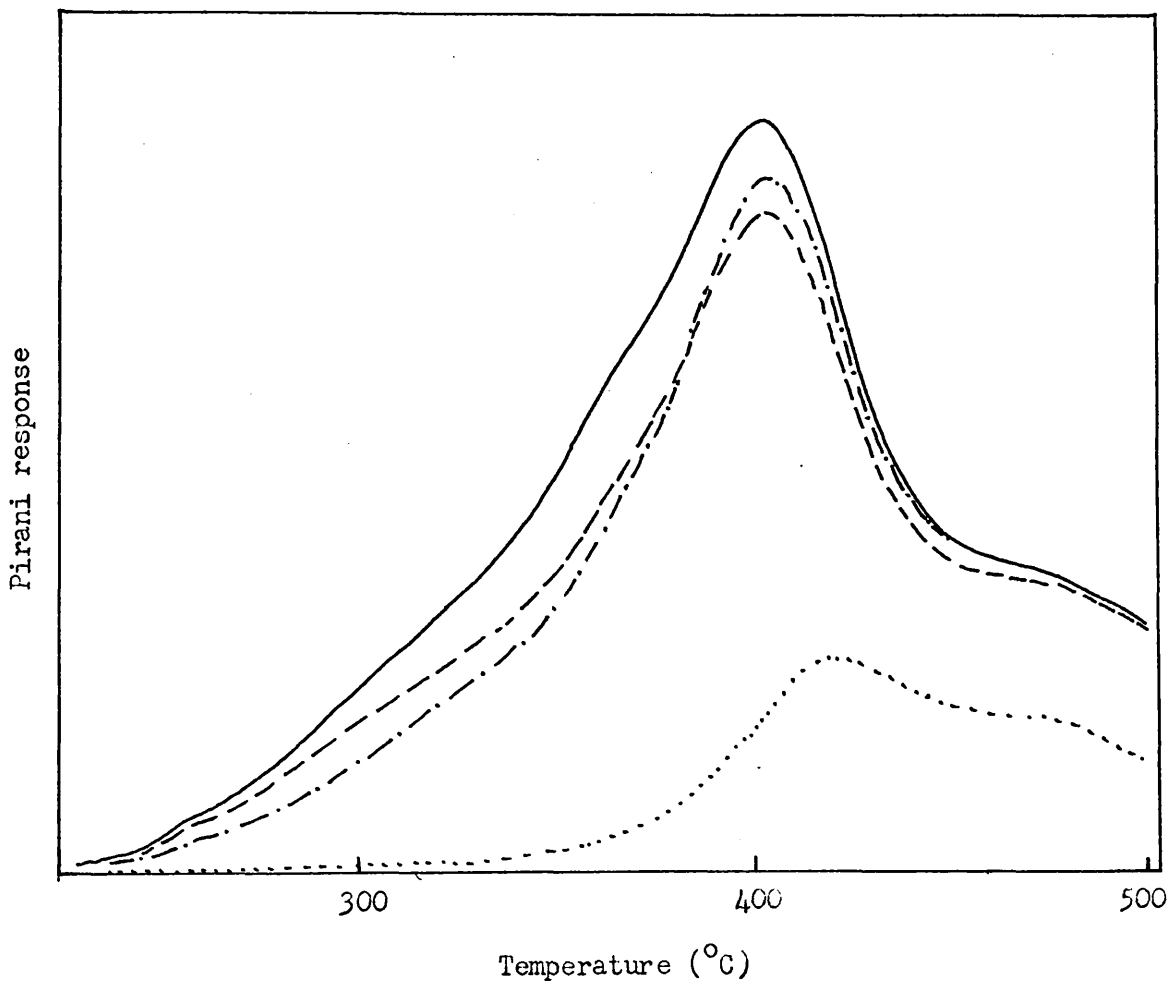


Fig. 4:11 TVA curve for 2·67% saponified copolymer

Trap Temperature (°C)

———— 0, -45

– – – – – – -75

—·—·—·—·— -100

..... -196°C

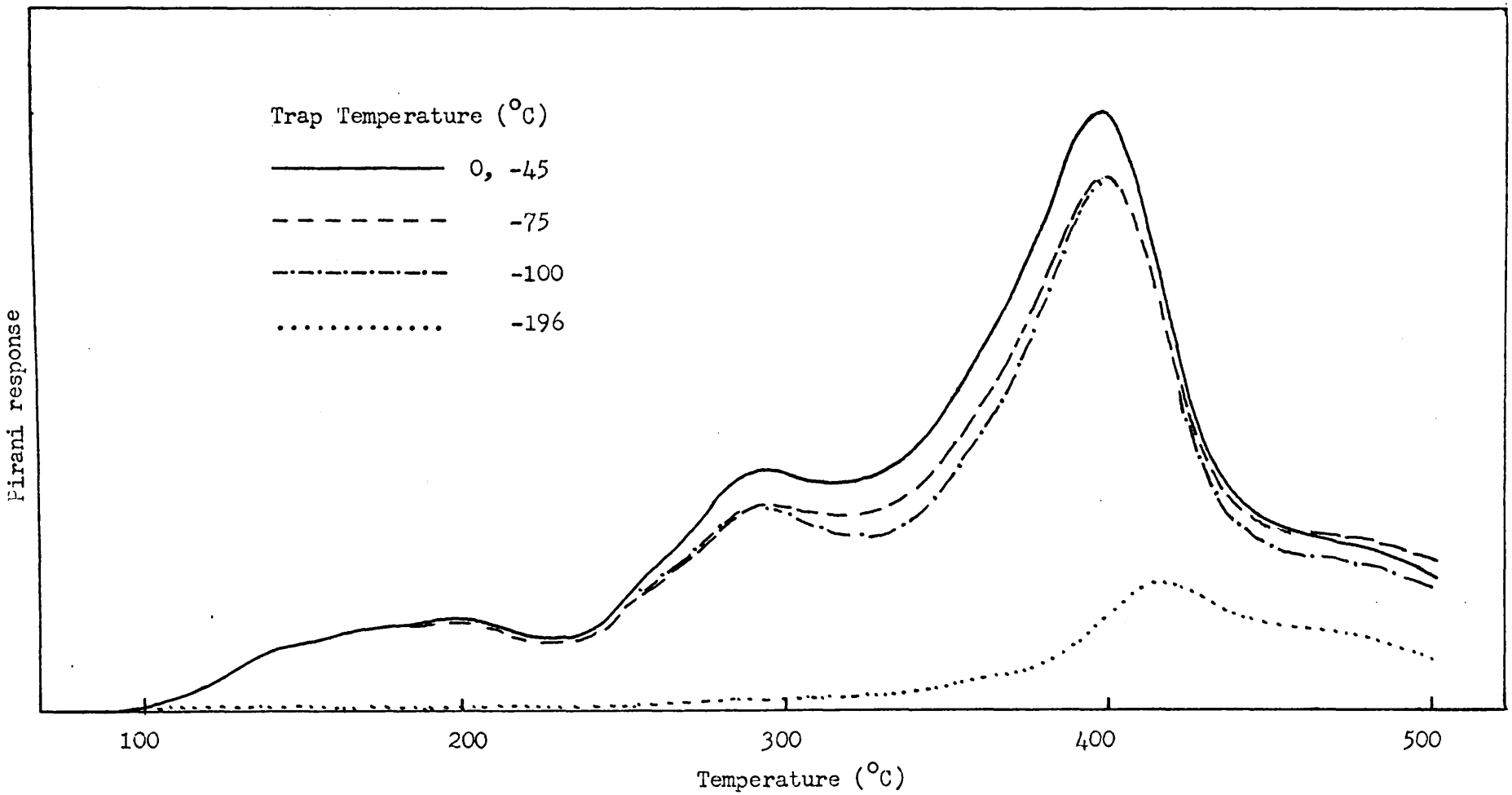


Fig. 4:12 TVA curve for 0.6% saponified copolymer.

pure PV-OAc.

In view of the fact that elimination of acetic acid from PV-OAc proceeds from units to unit along the chain, it may be that the greater stability of the copolymer is due to the reaction being blocked by V-OH units which means that each sequence of V-OAc unit requires its own initiation step. In none of the traces is there any limiting rate effect similar to that observed in the 0°C and -45°C curves of PV-OAc, since a sufficient quantity of acetic acid is not produced in the degradation of the copolymers.

In both types of copolymers (saponified and alcoholysed) at higher V-OH contents, water was formed principally in two stages namely, below 120°C and above 300°C. The water liberated at the latter temperature was thought to be the result of a dehydration reaction on the polymer chain, where as the former was considered to be water trapped in the polymer matrix.

Fig. 4:9 shows that two stages can be distinguished in the degradation of 53·19% copolymer. The first peak appears in the same temperature range as in the case of PV-OAc (Fig. 4:1), but its total area is smaller and the smaller distance between the -45°C and -75°C peaks, indicates a lower proportion of acetic acid. Analysis of the products associated with the first peak showed the presence of carbon dioxide, ketene, acetic acid and water.

Analysis of the products associated with the second peak indicates that they are carbon dioxide, with smaller amounts of methane, ethylene, and benzene.

From Fig. 4:10, it is obvious that 7·72% copolymer degrades in four stages, the first two peaks with T_{max} 324°C and 368°C respectively corresponds to acetic acid elimination. The third TVA peak has a T_{max} of 385°C. The Pirani response at this peak is mainly due to water and

acetaldehyde. Some non-condensable products are also trapped at -196°C. The fourth peak gives T_{max} at 480°C. This high temperature peak results from products, a large proportion of which are non-condensable at -196°C and which are formed by break up of the unsaturated polyene chains.

Two stage degradation of 2·67% copolymer is shown in Fig. 4:11 the initial peak due to acetic acid being almost disappeared.

In the trace of 0·6% copolymer shown in Fig. 4:12, the first low broad peak has a T_{max} around 150°C and the behaviour in the -75°C is characteristic of water in the TVA system [66]. Because water is used as solvent for the copolymer, it is difficult to distinguish between absorbed water and water being chemically eliminated. The second TVA peak has a T_{max} at 295°C. Some of the products are trapped at -75°C, some at -100°C but not at -196°C. Product analysis of this part of the trace showed the presence of water and smaller amount of acetic acid. The main degradation reaction is associated with the third peak which has a T_{max} at 400°C. The Pirani responses at this peak are mainly due to water and acetaldehyde. A very small amount of non-condensable products are also trapped at -100°C and -196°C. Formaldehyde [38] and hydrogen [40] have also been reported to be formed during the degradation but they were not observed in the present study. The remaining peak is due mainly to non-condensables and has T_{max} at 475°C. The existence of this high temperature peak is accounted for by break-down of the polyene structures as in the other copolymers.

TVA traces for three V-OAc/V-OH alcoholysed copolymers containing 40·54%, 24·03% and 1·646% V-OAc in the chain are shown in Fig. 4:13, 4:14 and 4:15 respectively. Their thermal degradation behaviour can be interpreted in the same way as described for saponified copolymers.

Values of T_{base} (the temperature at which the polymer starts degrading) and T_{max} (the temperature at which the rate of evolution is

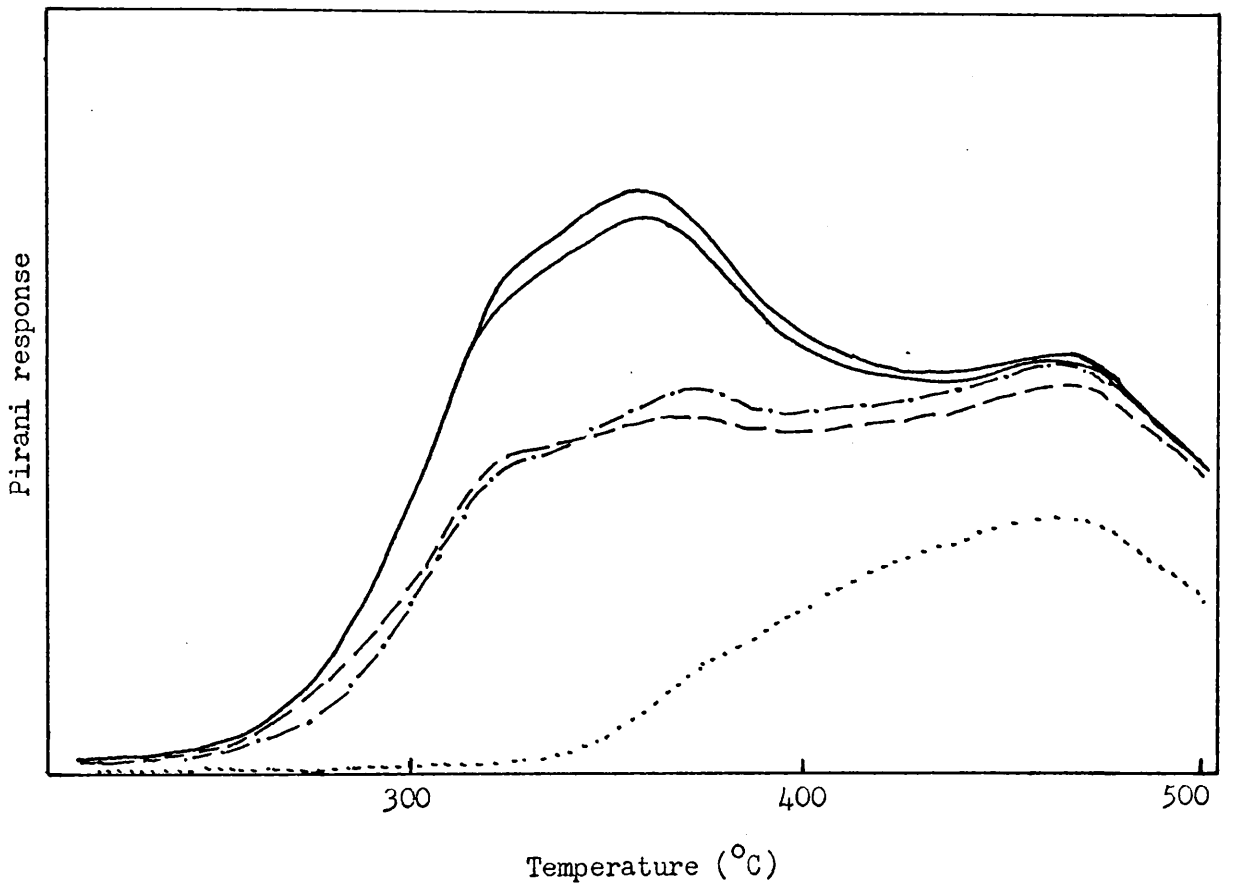


Fig. 4:13 TVA curve for 40·54% alcoholysed copolymer.

Trap Temperature (°C)

———— 0, -45

– – – – – – -75

—·—·—·—·— -100

..... -196

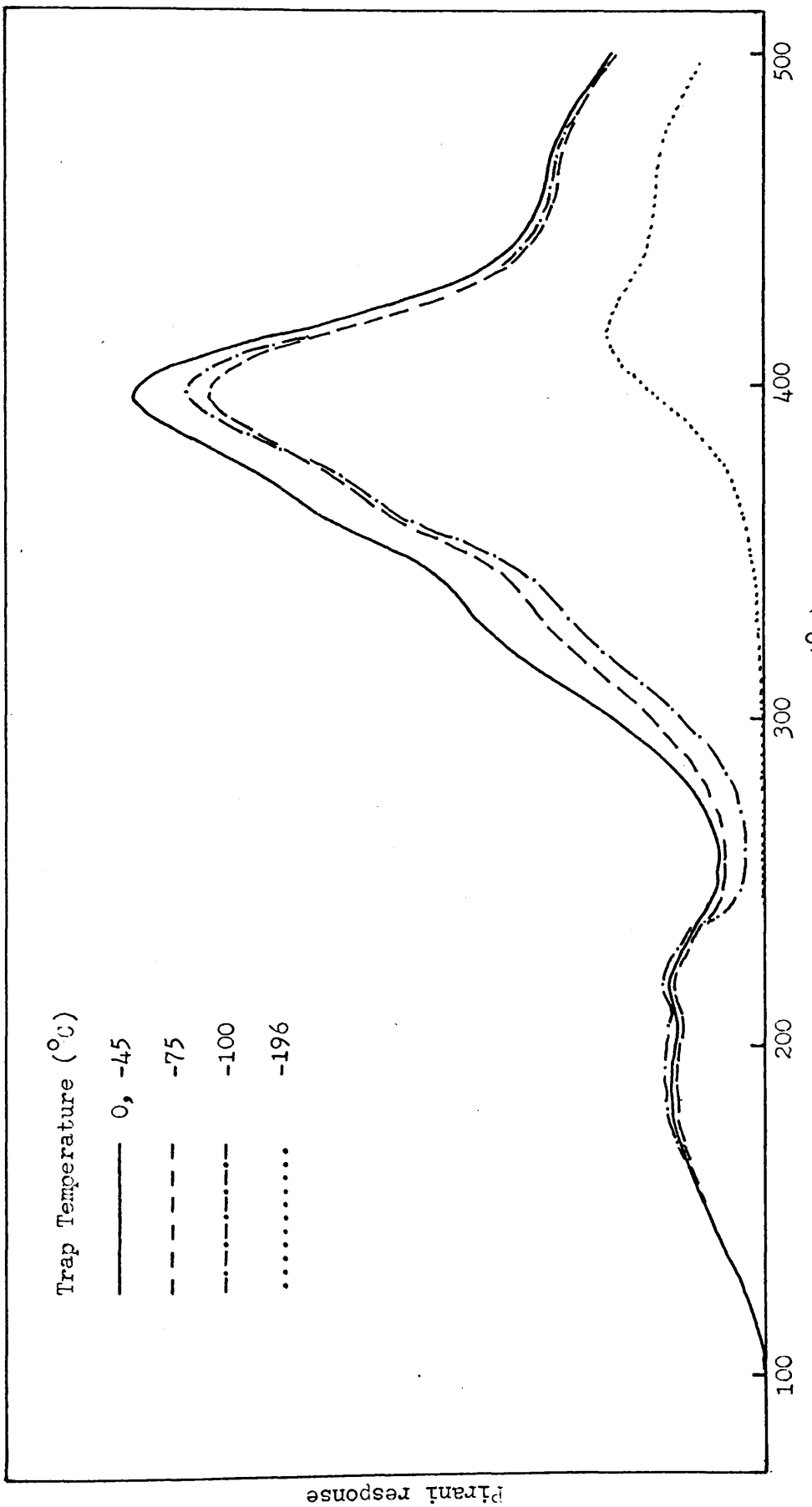


Fig. 4:14 TVA curve for 24.03% alcoholysed copolymer.

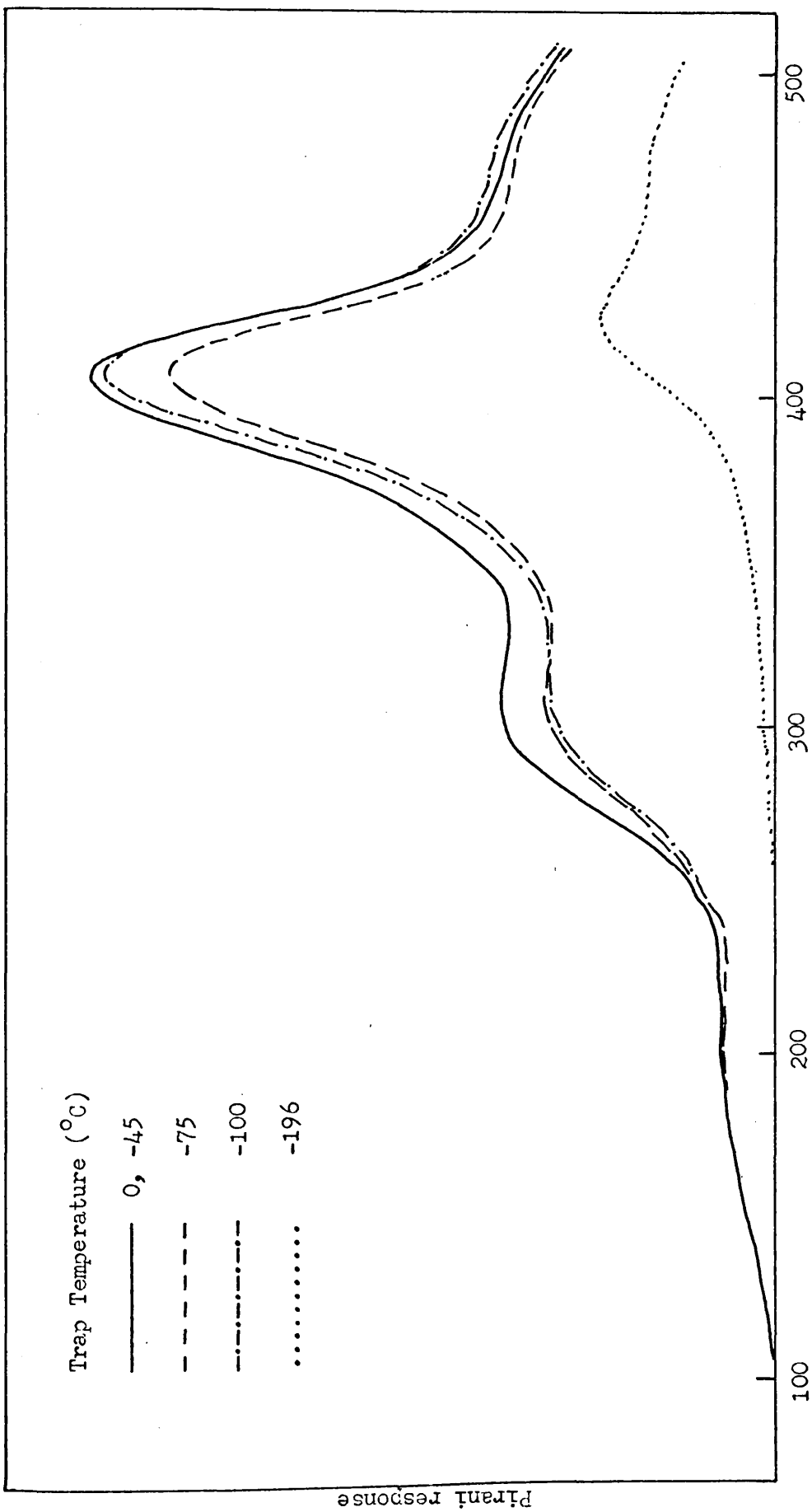


Fig. 4:15 TVA curve for 1·65% alcoholysed copolymer.

Table 4.3.

Details of TVA thermograms - Figures 4:9-4:15.

V-OAc/V-OH Copolymer V-OAc(mole%)	T_{base} (°C)	T_{max} (°C)			
		1st peak	2nd peak	3rd peak	4th peak
(A)					
53·19	232	-	355	-	480
7·72	232	324	368	385	480
2·67	235	-	-	400	480
0·6	100	295	-	400	480
(B)					
40·54	230	-	324	357	466
24·03	120	180	329	385	467
1·646	120	180	305	403	475

(A) Saponified Copolymers.

(B) Alcoholysed Copolymers.

a maximum) are summarised in Table 4.3.

C. Thermal Gravimetric Analysis.

TG traces for eight V-OAc/V-OH copolymers containing 53·19%, 19·9%, 7·72% and 0·6% V-OAc (saponified copolymers); and 40·54%, 24·03%, 10·4% and 1·646% V-OAc (alcoholysed copolymers) in the chain are reproduced in Fig. 4:16 and 4:17 respectively. For the copolymers there are two regions of weight loss corresponding to the breakdown of V-OAc amd V-OH units, the latter breakdown occurring at slightly higher temperatures.

Also, as expected from TVA results, as the V-OAc content of the copolymers increases, the stability to weight loss decreases. The threshold degradation temperature (T_{base}) does not change significantly with composition but the TG curves diverge considerably in the range 275-375°C. Weight loss from the alcohol rich polymers at lower temperatures is considered to be the result of the elimination of water trapped in the copolymer matrix.

The yield of residue at 500°C does not differ significantly from that formed on decomposition of the homopolymer. For each of the copolymers the percentage residue from degradation under nitrogen is higher than from degradation under vacuum. This difference is attributed to the short chain fragments which escape from the hot zone under high vacuum conditions, but fail to do so under nitrogen, probably ultimately breaking down thermally to lower molecular weight products.

The copolymers are less stable to weight loss than the homopolymer below 340°C but at higher temperatures the weight loss is less.

Weight loss data at various temperatures, derived from the TG data are presented in Tables 4.4 and 4.5.

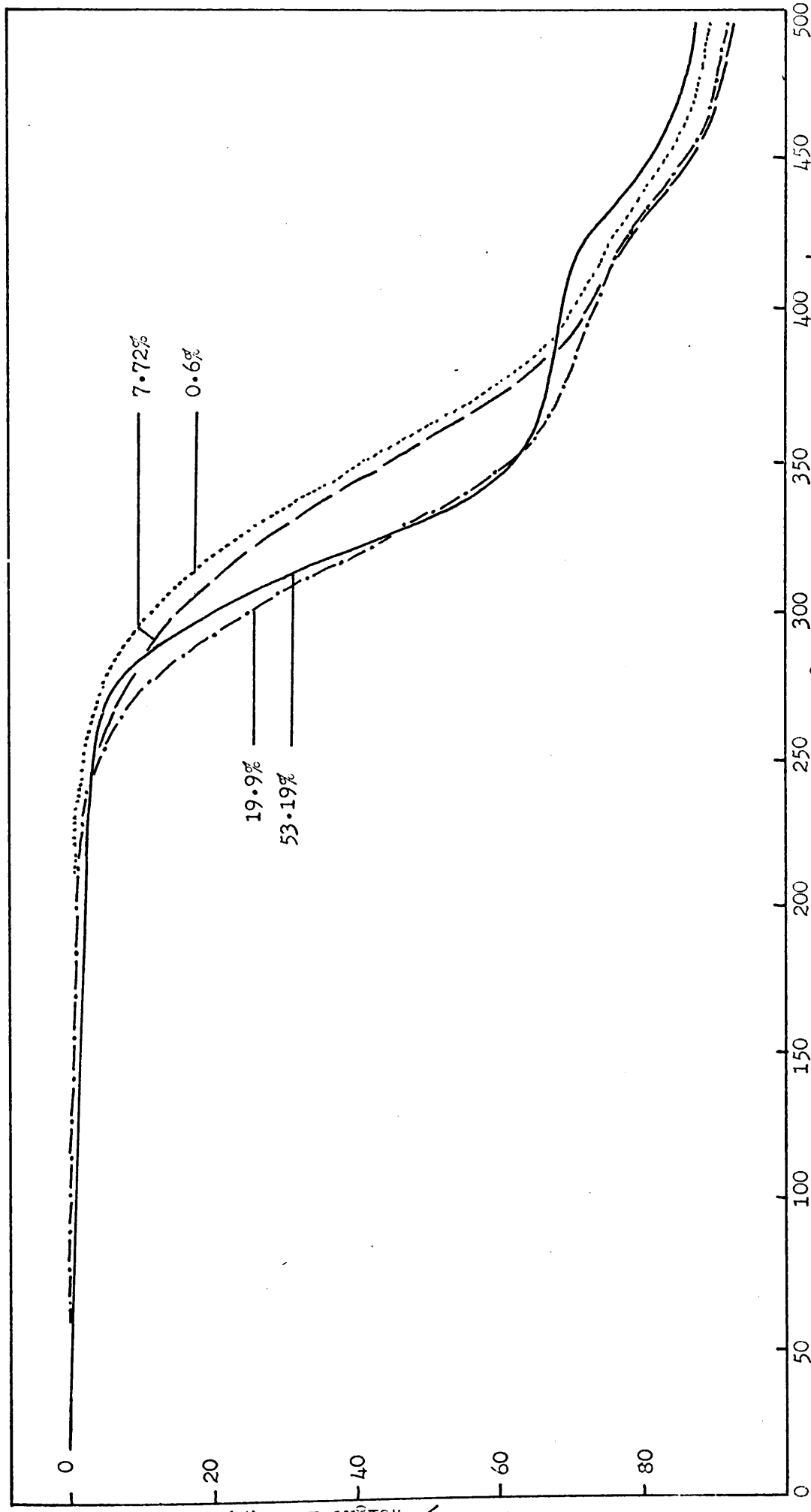


Fig. 4:16 TG curves for saponified V-OAc/V-OH copolymers, sample size 5 mg, Dynamic N_2 atmosphere, Heating rate 10°/min.

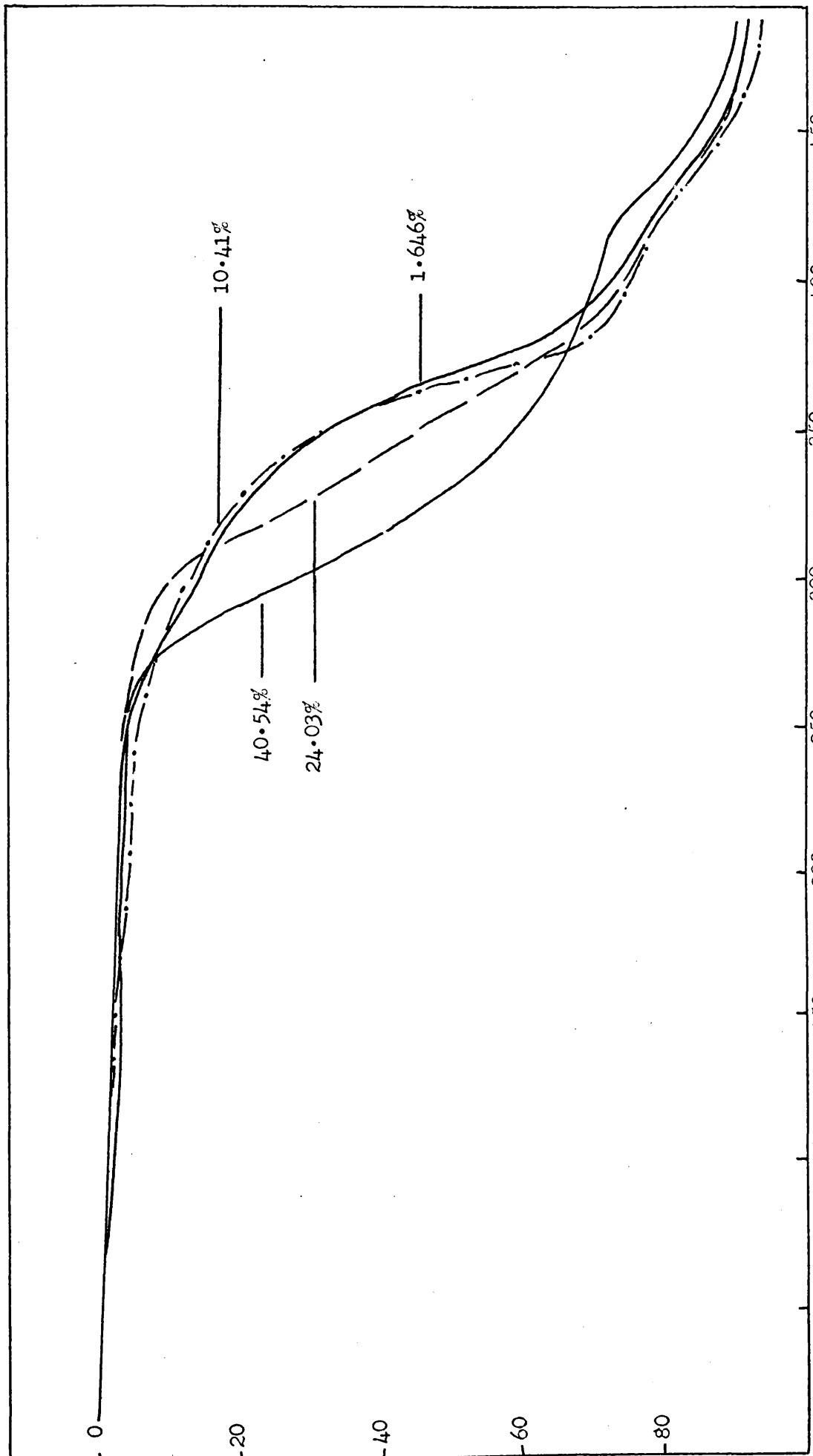


Fig. 4:17 TG curves for alcoholysed V-OAc/V-OH copolymers. Sample size 5 mg, Dynamic N_2 atmosphere, Heating rate 10°/min.

Percentage Weight loss data for saponified and alcoholysed copolymers at various temperatures under N_2 and vacuum.

Table 4.4.

Saponified Copolymers V-OAc (mole %)	% Weight loss at temperature				
	300°C	350°C	400°C	450°C	500°C
	N_2	N_2	N_2/Vac	N_2/Vac	N_2/Vac
53·19	19	63	69/69	81/86	88/95.5
19·9	20	61	73·5	86	92
7·72	16	45	73·0	86	92
0·6	11	41	70·5/82	84/91	94·5/95

Table 4.5.

Alcoholysed Copolymer V-OAc (mole %)	% Weight loss at temperature				
	300°C	350°C	400°C	450°C	500°C
	N_2	N_2	N_2/Vac	N_2/Vac	N_2/Vac
40·54	26	59	70·5	85	92
24·03	10	45	75/77	88/93	93/97
10·41	13	31	75	88	94
1·646	13	31	73/78	87/91.5	93/96·5

The loss in weight of the 53·19% saponified and 40·54% alcoholysed copolymers which occurs during isothermal heating under nitrogen was investigated at different temperatures and the results are presented in Figs. 4:18 and 4:19. The energies of activation of the thermal decomposition of saponified and alcoholysed copolymers calculated from the initial slopes of the curves in figures 4:18 and 4:19 were found to be 30·3 and 22·4 kcals/mole respectively. Fig. 4:20 shows a typical Arrhenius plot.

D. Differential Thermal Analysis.

DTA traces for V-OAc/V-OH copolymers containing 53·19%, 19·9%, 7·72% and 0·6% V-OAc (saponified copolymers) and 40·54%, 24·03%, 10·4% and 1·646% V-OAc (alcoholysed copolymers) are shown in Figs. 4:21 and 4:22 respectively. The endotherms in the region 172 - 231°C are associated with melting, the sharpening of the endotherms with increasing alcohol content reflecting the greater crystallinity of PV-OH compared with PV-OAc. Degradation is reflected by the endotherms and exotherms at higher temperatures, the endotherms are probably associated with the breakdown of acetate and alcohol units while the exotherms are probably associated with cyclisation processes.

The melting points (T_m) of the various copolymers are summarised in Table 4.6 and plotted as a function of composition in Fig. 4:23. The melting points of the copolymers are obviously not a simple function of the composition, and also depend upon the method of preparation of the copolymers. The fact that the curve in Fig. 4:23 for the saponified copolymer is consistently above that of the alcoholysed copolymer may be an indication that PV-OH prepared by saponification is more highly crystalline than that prepared by alcoholysis.

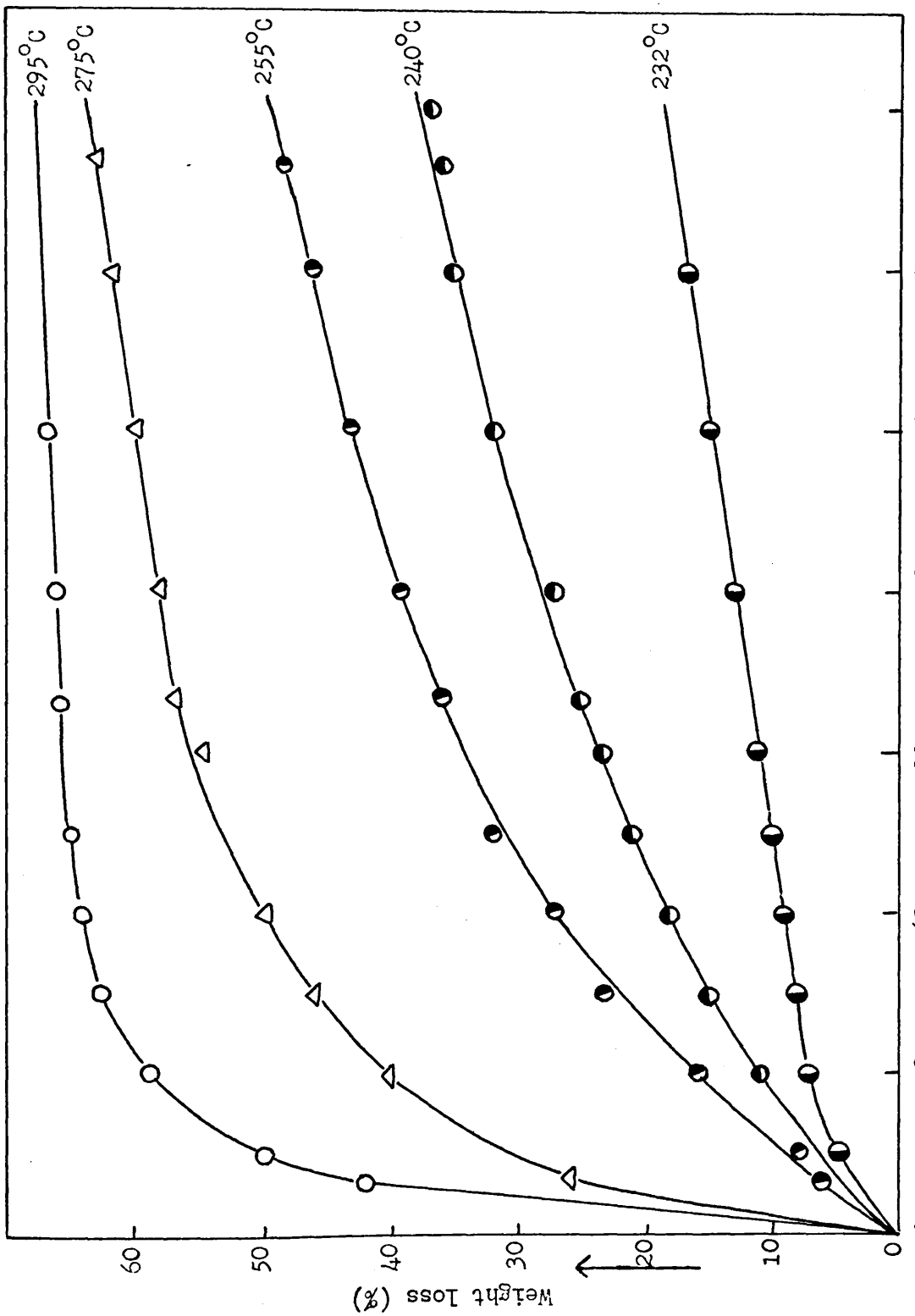


Fig. 4:18 Weight loss of 53·19 % Saponified copolymer as a function of time at various temperatures.

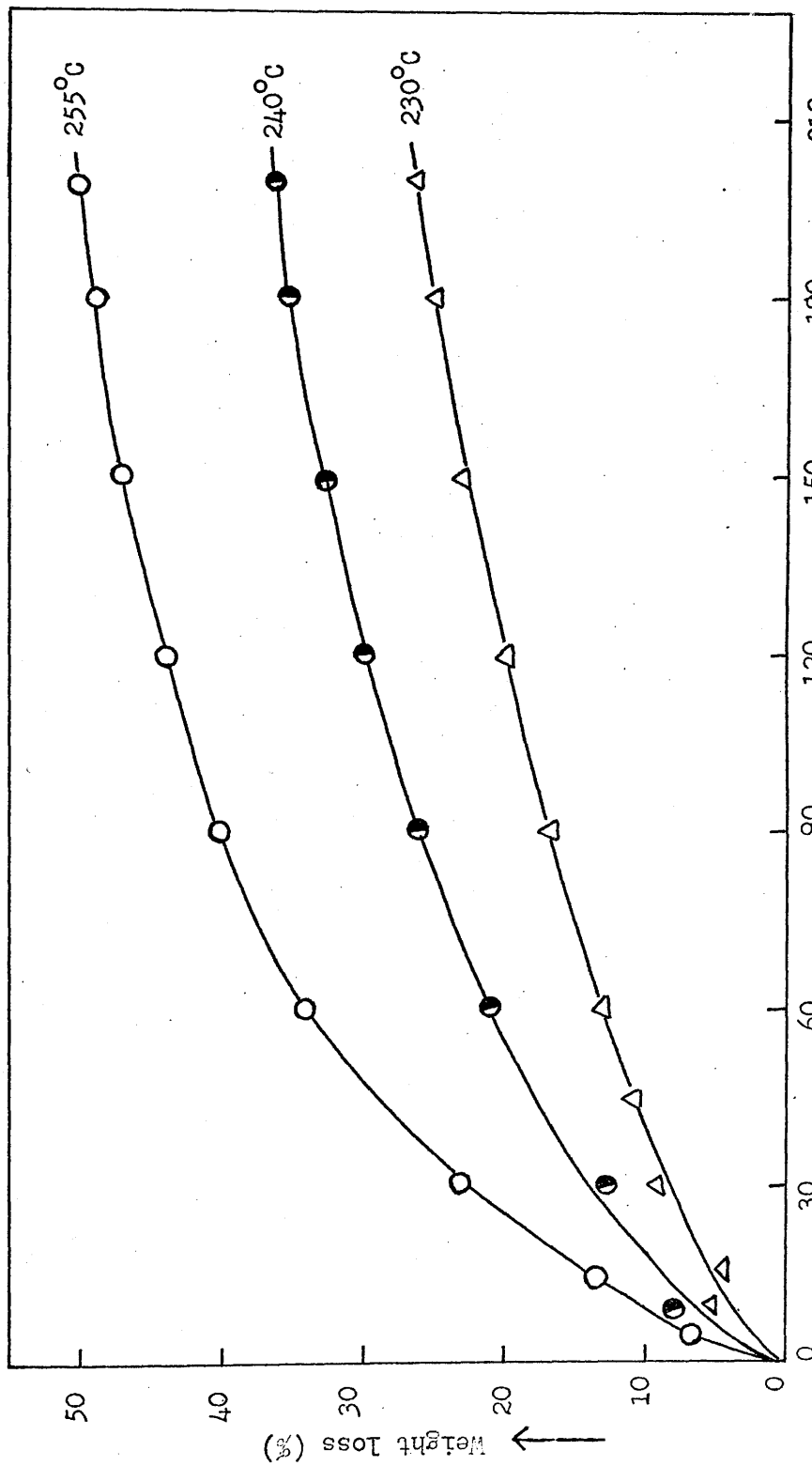


Fig. 4:19 Weight loss of 40·56% alcoholysed copolymer as a function of time at various temperatures.

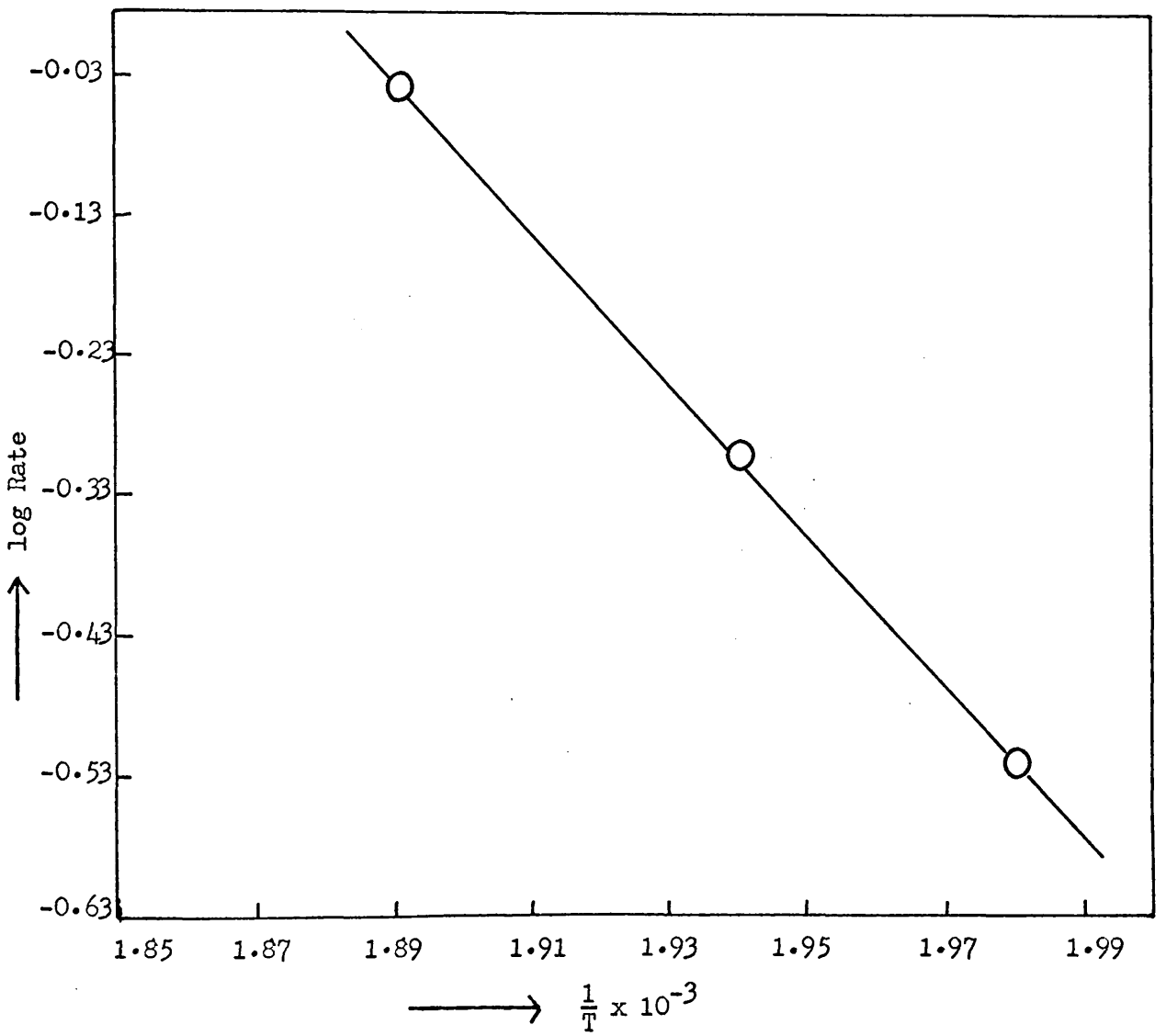


Fig. 4:20 Determination of the energy of activation for alcoholysed copolymer (V-OAc mole %) = 40·54% by plotting values of log Rate versus $\frac{1}{T}$ °k (the Arrhenius plot).

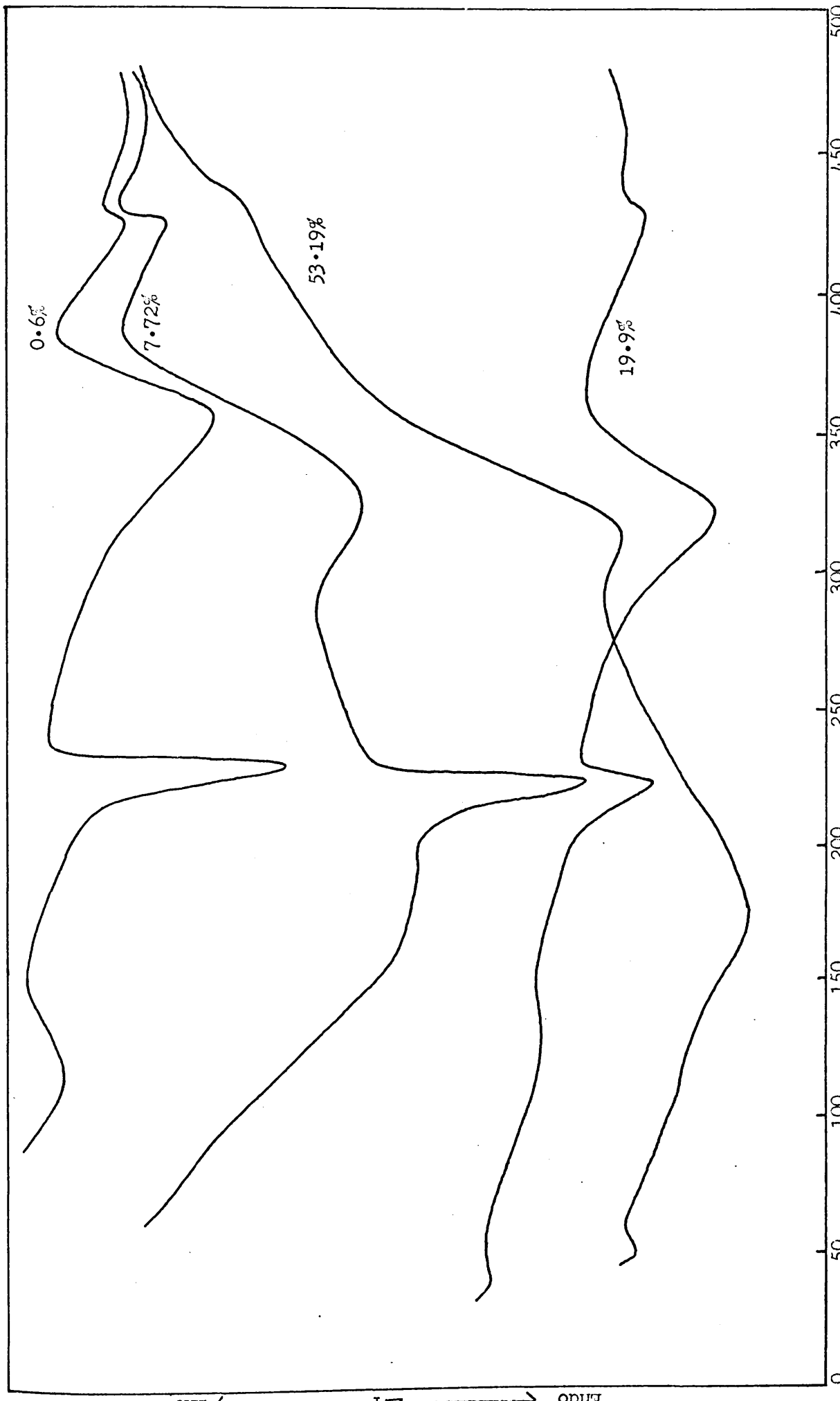


Fig. 4:21 DTA curves for saponified V-OAc/V-OH copolymers, sample size 10 mg, Dynamic N_2 atmosphere, Heating rate 10°/min

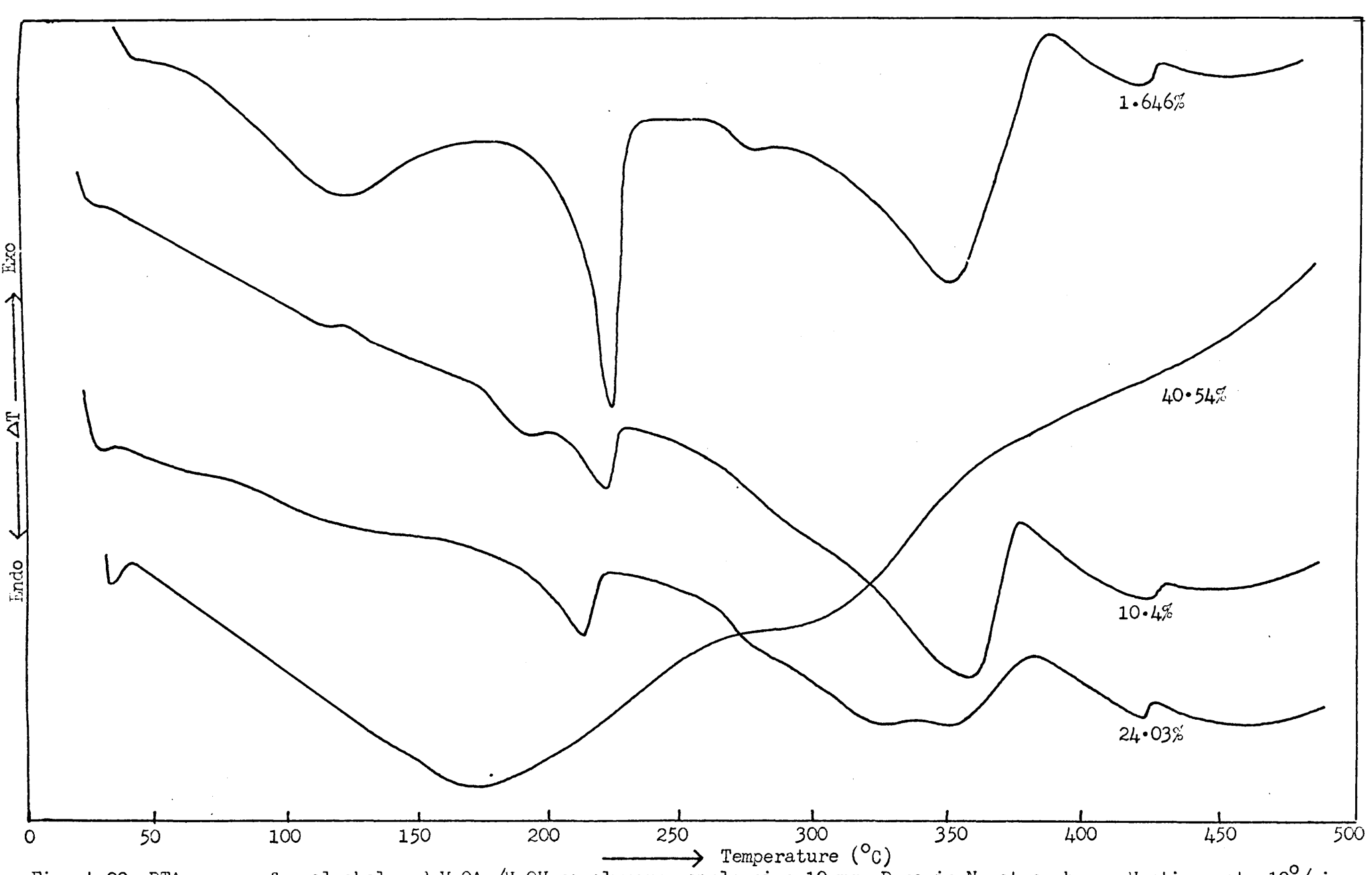


Fig. 4:22 DTA curves for alcoholysed V-OAc/V-OH copolymers, sample size 10 mg, Dynamic N_2 atmosphere, Heating rate 10°/min.

Table 4.6.

Melting point (Tm) data for V-OAc/V-OH Copolymers.

Saponified Copolymers		Alcoholysed Copolymers	
V-OAc (mole %)	Tm (°C)	V-OAc (mole %)	Tm (°C)
53·19	172	40·54	172
19·9	224	24·03	215
7·72	229	10·4	223
0·6	231	1·646	227

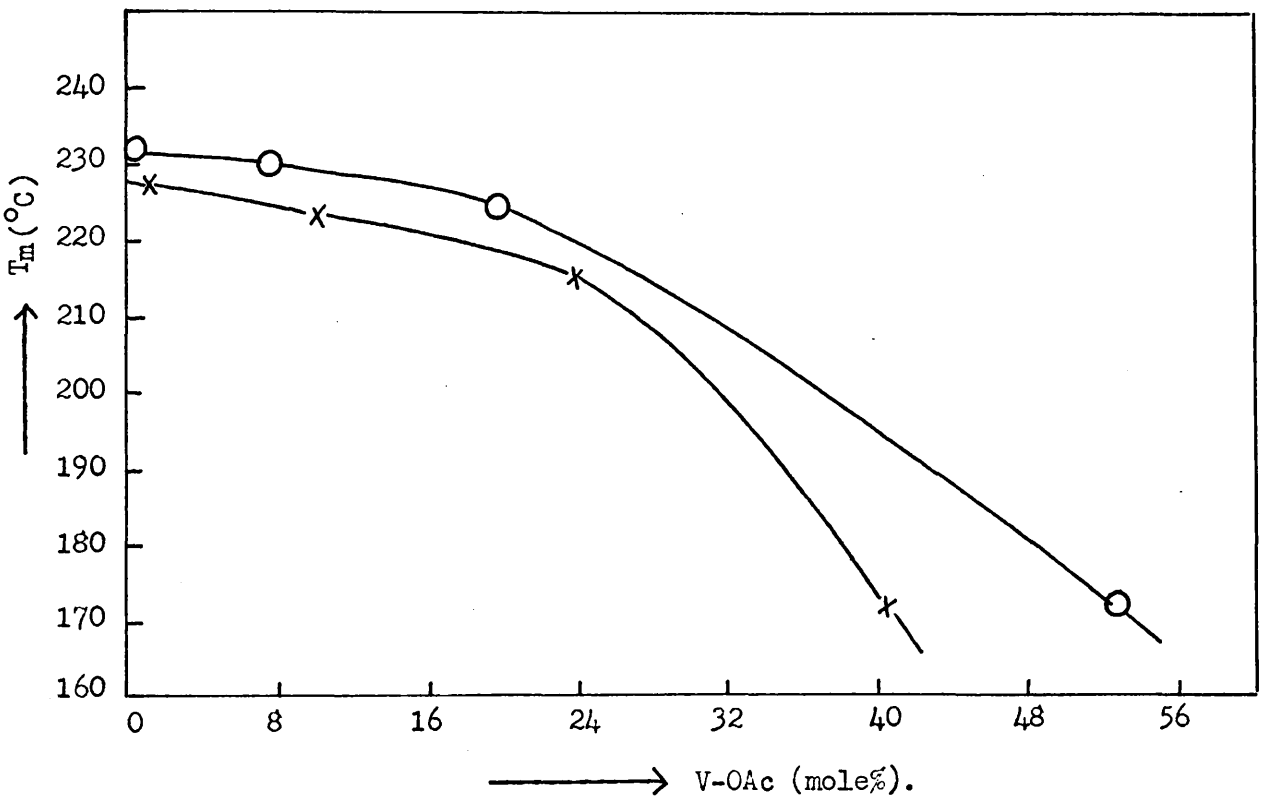
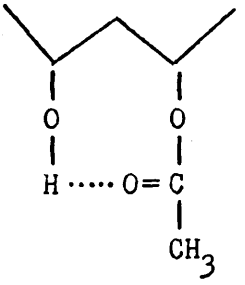


Fig. 4:23 T_m plots of V-OAc/V-OH copolymers as a function of composition.

—O— Saponified copolymers

—x— Alcoholysed copolymers

This in turn may be related to the fact that these are block rather than random copolymers [15,17,90]. Copolymers with higher melting points should thus be expected to have longer sequences of V-OH units than in a random distribution and should have fewer adjacent V-OH-V-OAc pairs. It has been shown that the enhanced reactivity of an acetate, which is adjacent to a hydrolysed group favours the formation of long sequence of V-OH units during alcoholysis and saponification. The reactivity is enchanced more in saponification than in alcoholysis and thereby longer sequence of V-OH units should be obtained by the former reaction. The partially saponified products are higher melting and have fewer V-OH-V-OAc pairs than the partially alcoholysed samples.



E. Product Analysis.

(a) I.R. Analysis of Volatiles. I.R. spectra of the volatiles from the various copolymers are almost identical differing only in the relative amounts of individual products. Typical i.r. spectra of the volatile products obtained from the degradation of 53·19% saponified copolymer and 24·03% alcoholysed copolymer are shown in Figs. 4:24 and 4:25 respectively.

Absorptions at 2300 - 2330 cm^{-1}, 721 cm^{-1} and below 700 cm^{-1} are attributed to carbon dioxide. Ketene is identified by its triplet peaks at 2120 - 2130 cm^{-1}. Absorption at 1780, 1730 and 1295 cm^{-1} is due to acetic acid (vapour) and acetaldehyde.

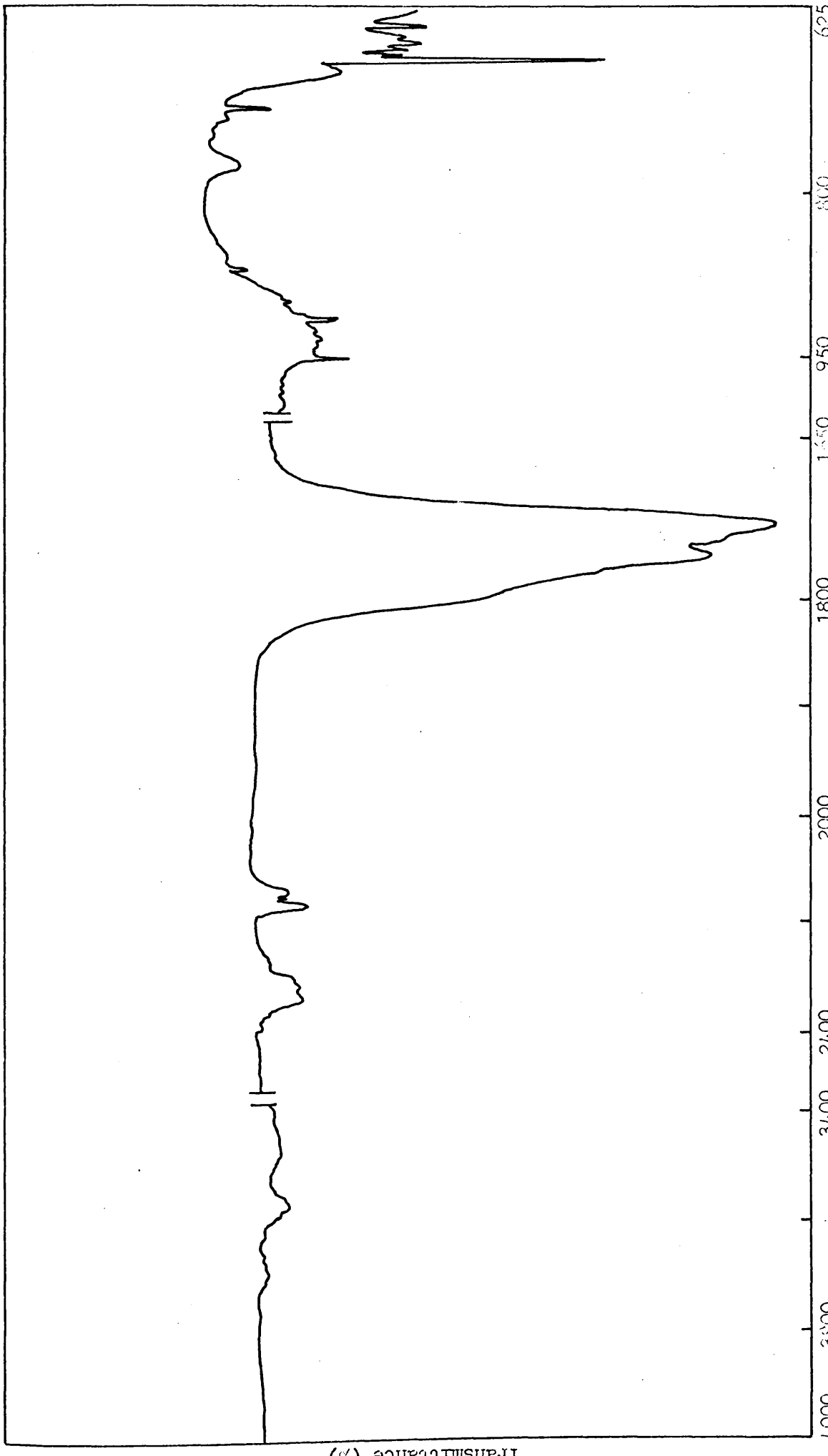


Fig. 4:24 I.R. Spectra of condensable degradation products from 53.19% saponified copolymer.

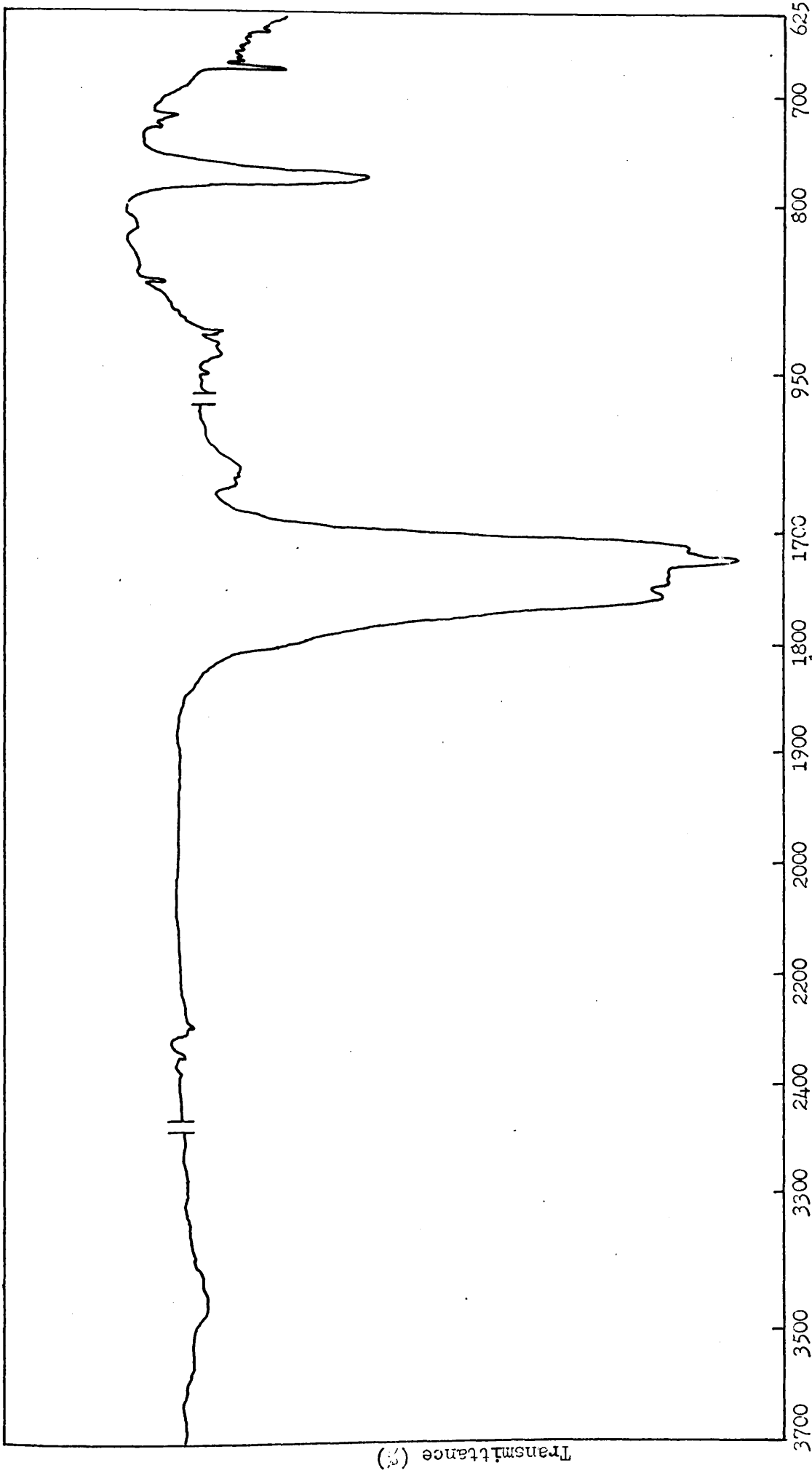


Fig. 4:25 I.R. Spectrum of the condensable degradation products of 24.03% alcoholysed copolymer.

Absorptions between 700 - 950 cm^{-1} are due to unsaturated hydrocarbons including ethylene. Absorption by water occurs at 3590 - 3650 cm^{-1}.

Examination of the I.R. spectra of the products from a number of copolymers show that absorbances in the regions associated with carbon dioxide and ketene increase with increasing V-OAc content in the copolymer. Copolymers containing as little as 1·65% V-OAc have been shown to evolve carbon dioxide as a decomposition product.

(b) I.R. Analysis of the Cold Ring Fraction. I.R. spectra of the yellowish-white cold ring fractions obtained from the copolymers after degrading to 500°C were run using the KBr technique and the regions of interest for 53·19%, 19·9% saponified copolymers and 24·03% alcoholysed copolymer are combined with the spectra of the original polymers and residues in Figs. 4:26, 4:27 and 4:28 respectively.

The main peaks observed were as follows,

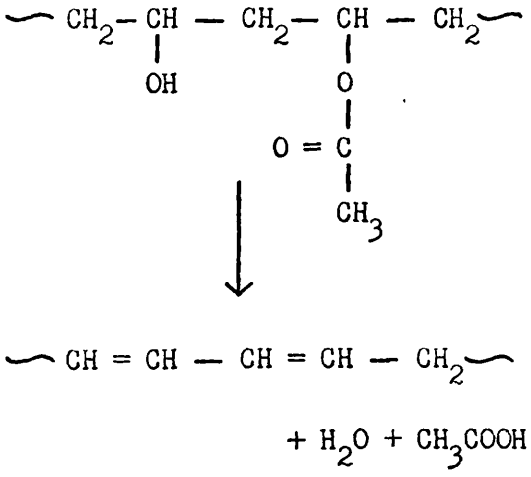
3020, 3060 cm^{-1}	-C = C-
2845, 2920 cm^{-1}	C - H stretching
1600 - 1610 cm^{-1}	-C = C-
1450 cm^{-1}	CH_2 bending
1375 cm^{-1}	$-CH_2-CH_2$ alkanes
815 cm^{-1}	C - H olefinic
880 cm^{-1}	C - H olefinic

The spectra of the C.R.F. are broadly similar to those of the parent copolymers but also reveal a number of new absorptions. The peak, a little above 3000 cm^{-1}, bands around 1600 cm^{-1} and in the 800 - 900 cm^{-1} regions arise from conjugation in the degraded

copolymers. The carbonyl absorptions of the acetate groups are present in the C.R.F. of the copolymers indicating that the C.R.F. contain some V-OAc units.

(c) I.R. Analysis of Residues. I.R. spectra of the black residues obtained from the same copolymers, after degrading to 500°C, were obtained. These are included in Figs. 4:26, 4:27 and 4:28 for comparison with that of the respective undegraded materials.

The i.r. absorptions contain the broad peaks associated with conjugation similar to those found in the C.R.F. No residual carbonyl and hydroxyl absorptions is observed in the residue which must therefore be largely composed of the long conjugated sequences resulting from complete elimination of water and acetic acid.



F. Quantitative Estimation of Acetic Acid and Water.

Fifty mg sample of 53·19% saponified and 40·54% alcoholysed copolymers were degraded under isothermal conditions at different temperatures in a closed evacuated system for various lengths of time; a liquid nitrogen trap was used to collect acid and water as they were formed and the acid was titrated against 0.01 M NaOH using

Fig. 4:26 I.R. Spectra of 53.19% saponified copolymer. (a) Undegraded copolymer, (b) C.R.F. of the copolymer degraded to 500°C (c) Residue of the copolymer degraded to 500°C.

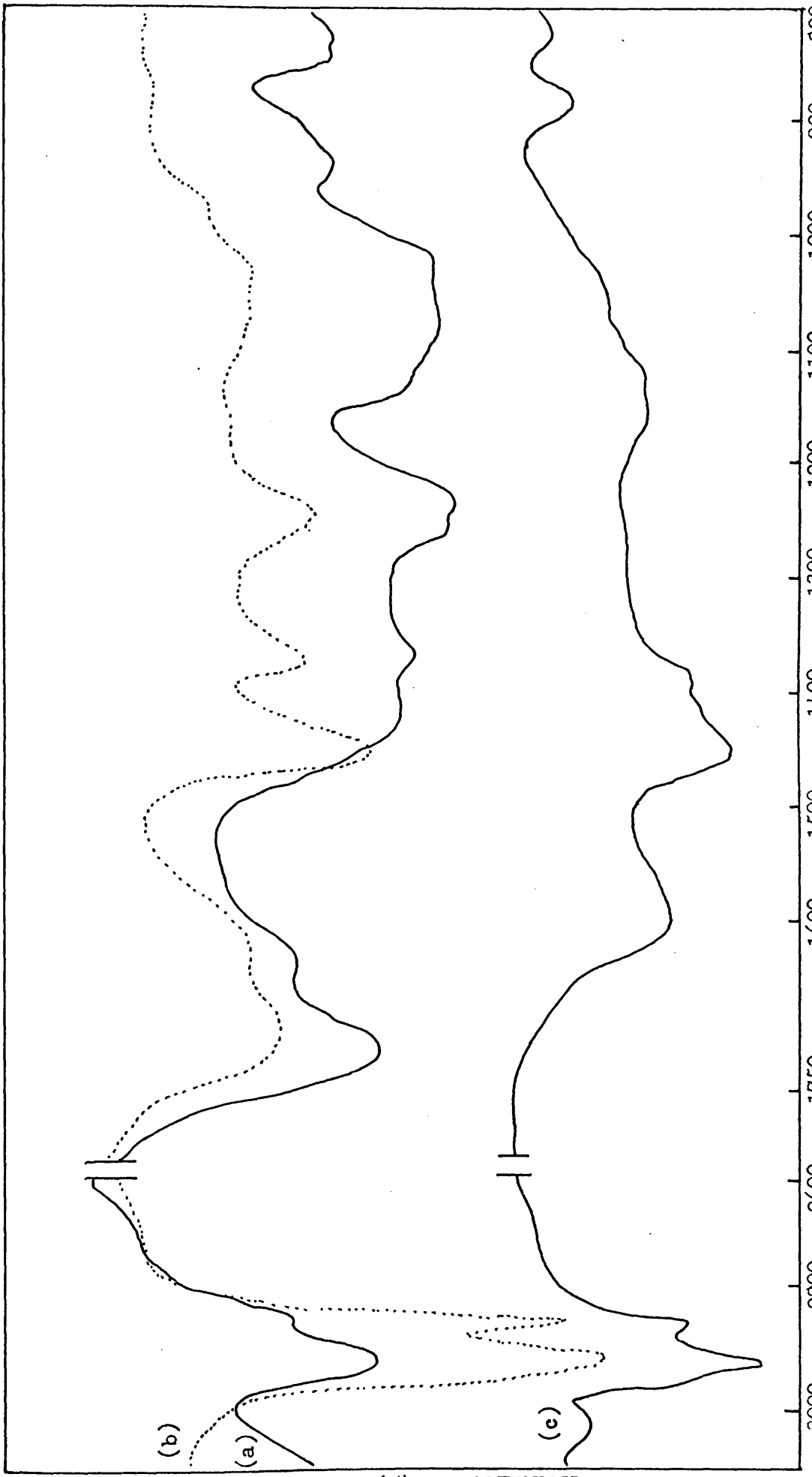


Fig. 4:27 I.R. Spectra of 19.9% saponified copolymer. (a) Undegraded copolymer, (b) C.R.F. of the copolymer degraded to 500°C, (c) Residue of the copolymer degraded to 500°C.

Fig. 4:28 I.R. Spectra of 24.03% alcoholysed copolymer. (a) Undegraded copolymer, (b) C.R.F. of the copolymer degraded to 500°C, (c) Residue of the copolymer degraded to 500°C.

phenolphthalein as an indicator. The weight of water was calculated by subtracting the weight of acid from the total weight of acid and water. The results of this investigation are shown in Figs. 4:29 a, b; 4:30, 4:31 and in Tables 4.7 and 4.8. It was also shown at this point that acetic acid has no influence on the rate of the reaction by repeating some of these reactions but placing the cold trap in position to collect the products only at the end of the degradation reaction. The results in Tables 4.7 and 4.8 show that acetic acid and water are not produced in the same ratio as they are present in the copolymers. It is not possible, however, to say whether this is in any way associated with reaction mechanism because a certain amount of water, impossible to estimate precisely, is also physically absorbed on the polymer. Thus one can only compare the degradation of the two copolymers on the basis of acetic acid production. Fig. 4:32 shows that acetic acid evolution in saponified copolymer is higher than in alcoholysed copolymer at the higher temperatures. The higher yield of acid from the former may be associated with the different tendencies to blocking in copolymers prepared by the two methods. This will be discussed later in more detail in section 2 H. This is clearly also associated with the differences in T_m already discussed in section 2 D.

G. Structural Changes During Degradation.

Before discussing the detailed mechanism of the degradation of the copolymer system, it is of interest to consider the possibility of interaction between adjacent acetate and alcohol units in the chain. In particular it was considered that a reaction sequence of the following type might be possible,

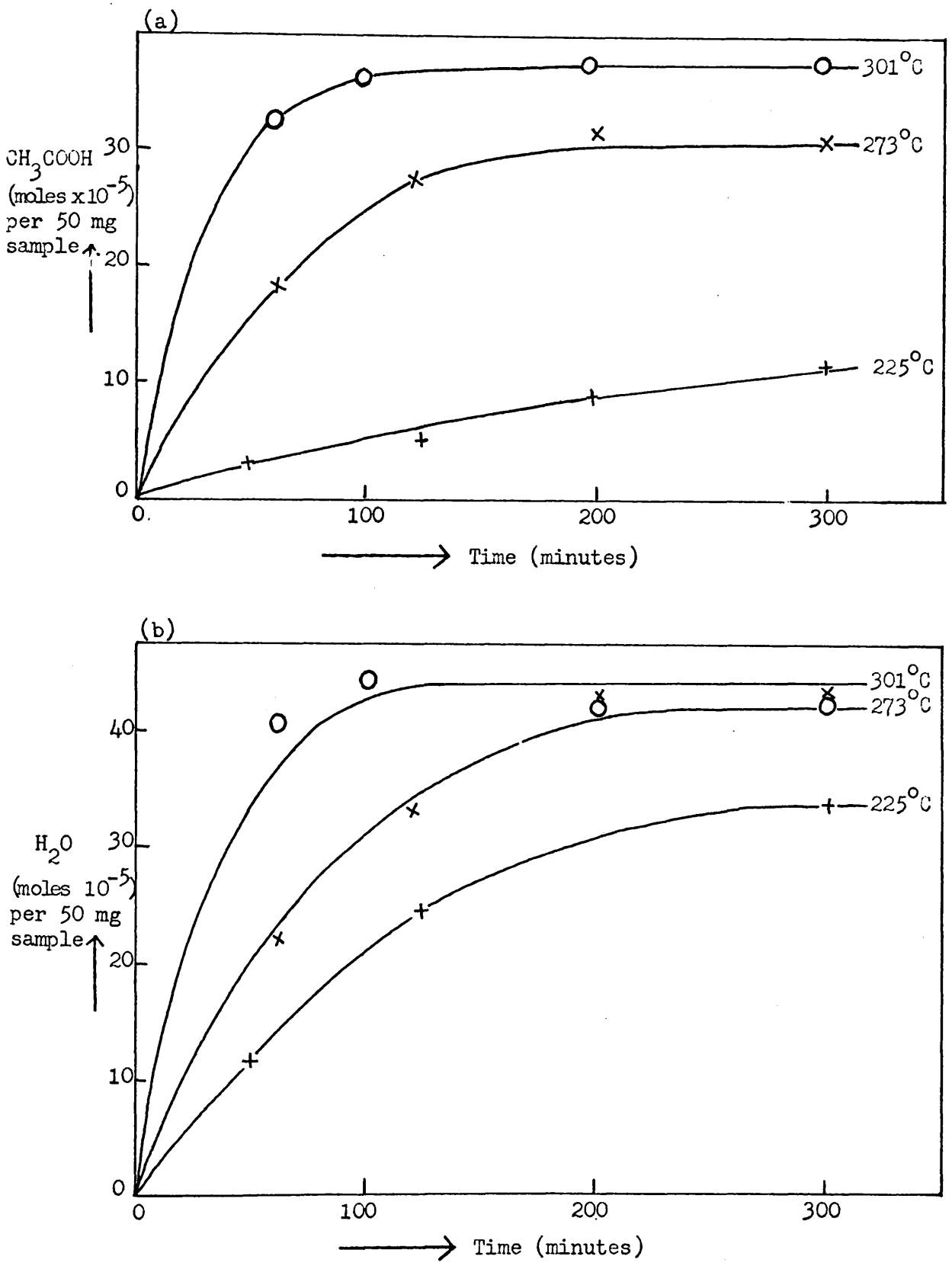


Fig. 4:29 Acetic acid and water evolution from 53·19% saponified copolymer.

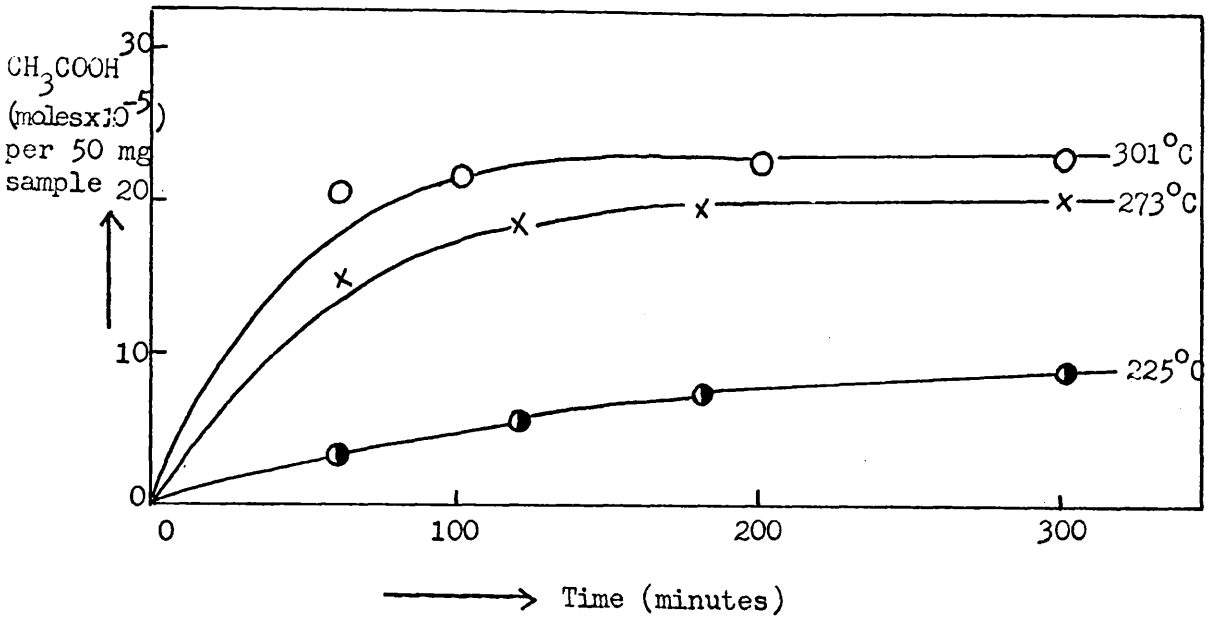


Fig. 4:30 Acetic Acid evolution from 40.54% alcoholysed copolymer.

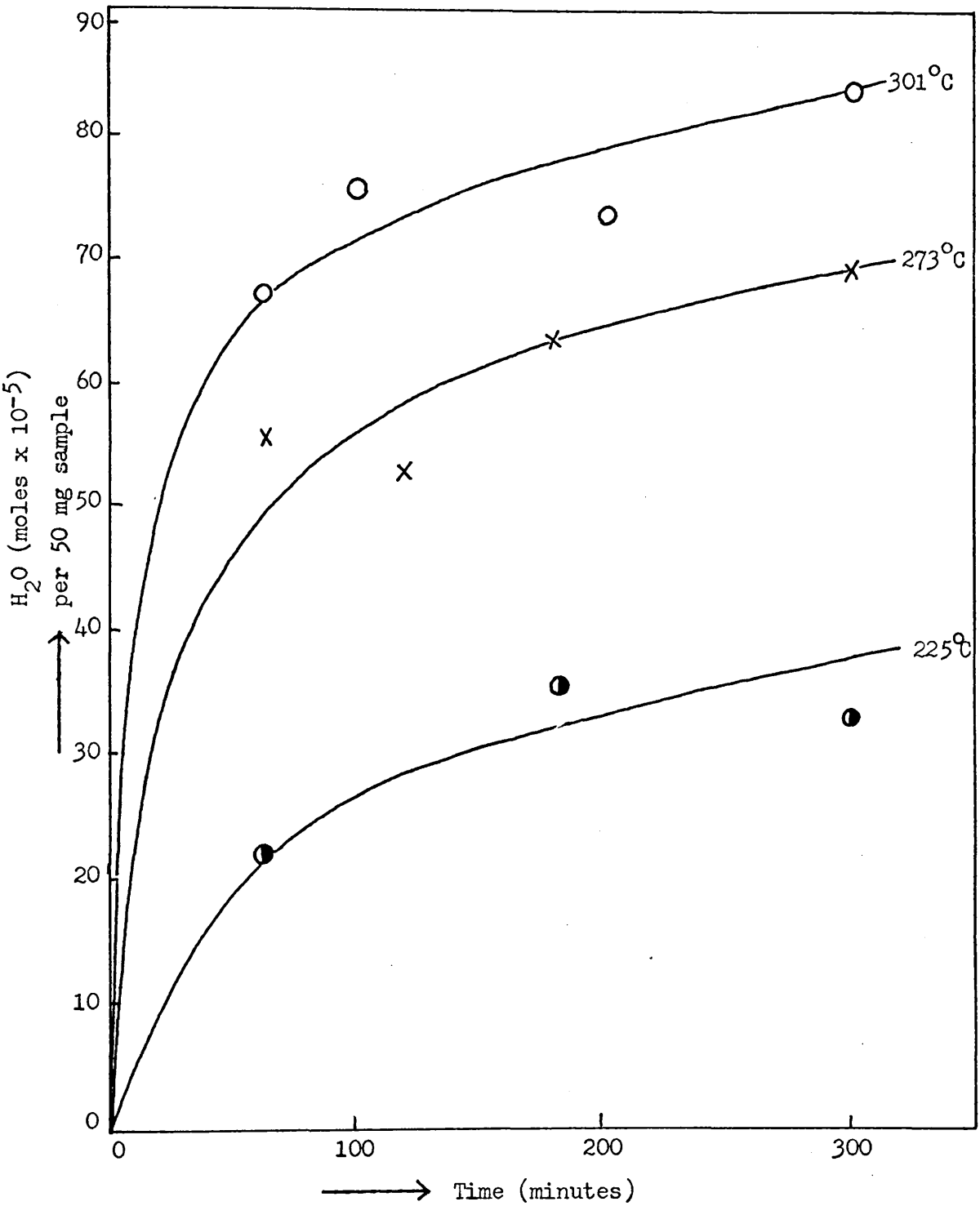


Fig. 4:31 Water evolution from 40·54% alcoholysed copolymer.

Degradation Temperature (°C)	Degradation Time (Min)	53·19% Saponified Copolymer		Degradation Time (Min)	40·54% Alcoholysed Copolymer	
		CH_3COOH (moles x 10^{-5})	H_2O (moles x 10^{-5})		CH_3COOH (moles x 10^{-5})	H_2O (moles x 10^{-5})
225	50	2·9	11·44	60	3·00	22·77
	125	4·833	24·33	120	5·5	-
	200	8·9	24·33	180	7·0	36·11
	300	11·1	33·55	300	8·5	33·33
273	60	17·6	21·88	60	14·7	56·55
	120	27·4	33·11	120	18·0	-
	200	31·3	42·33	180	19·0	63·88
	300	30·8	43·44	300	20·1	69·83
301	60	33·2	41·11	60	20·6	67·22
	100	36·5	45·00	100	21·7	76·00
	200	37·3	42·77	200	22·4	73·66
	300	37·4	42·00	300	22·6	83·55

Table 4.7. Acetic acid and water evolution per 50 mg sample degraded in vacuum under isothermal conditions.

53·19% Saponified Copolymer				40·54% Alcoholysed Copolymer		
Degradation Temperature (°C)	Degradation Time (Min)	Copolymer (molar ratio)	CH_3COOH, H_2O (molar ratio)	Degradation Time (Min)	Copolymer (molar ratio)	CH_3COOH, H_2O (molar ratio)
225	50	1·14	0·253	60	0·682	0·1317
	200	"	0·365	180	"	0·193
	300	"	0·330	300	"	0·255
273	60	1·14	0·804	60	0·682	0·259
	120	"	0·827	180	"	0·287
	200	"	0·739	300	"	0·288
301	60	1·41	0·807	60	0·682	0·306
	100	"	0·811	100	"	0·285
	200	"	0·872			
	300	"	0·890	200	"	0·304

Table 4.8. Acetic acid and water evolution per 50 mg sample degraded in vacuum under isothermal conditions.

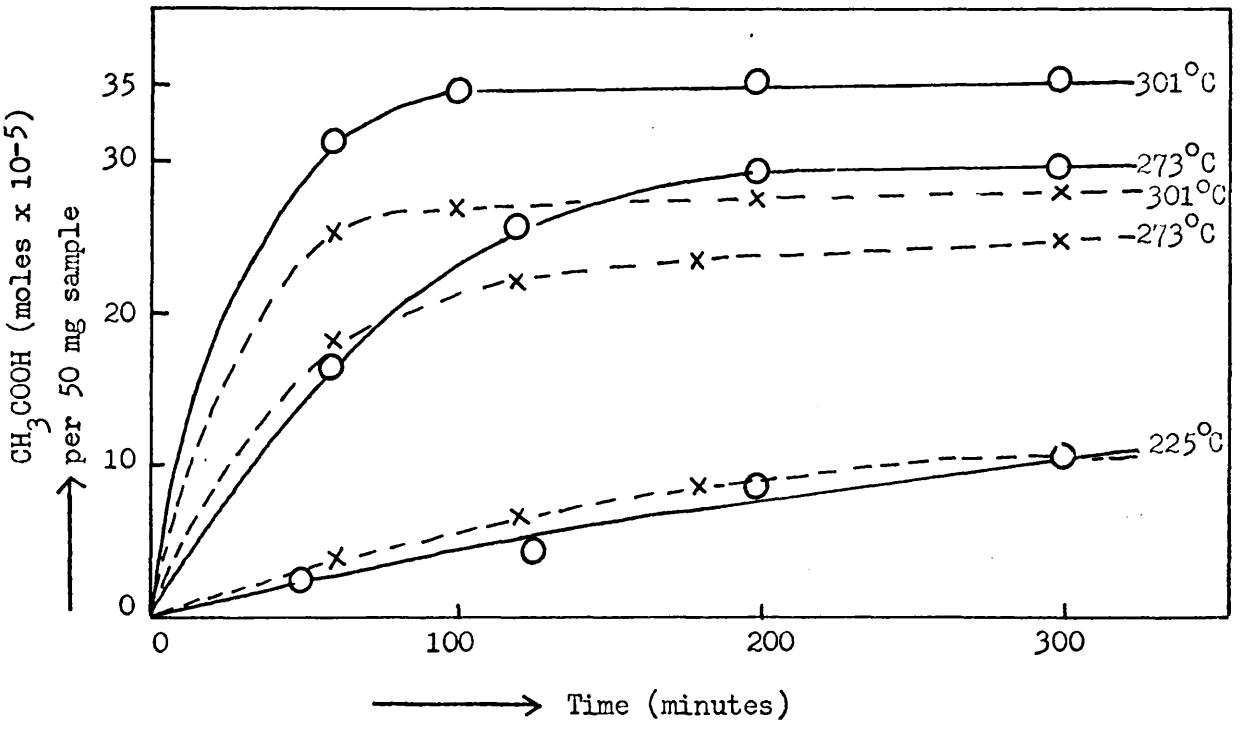
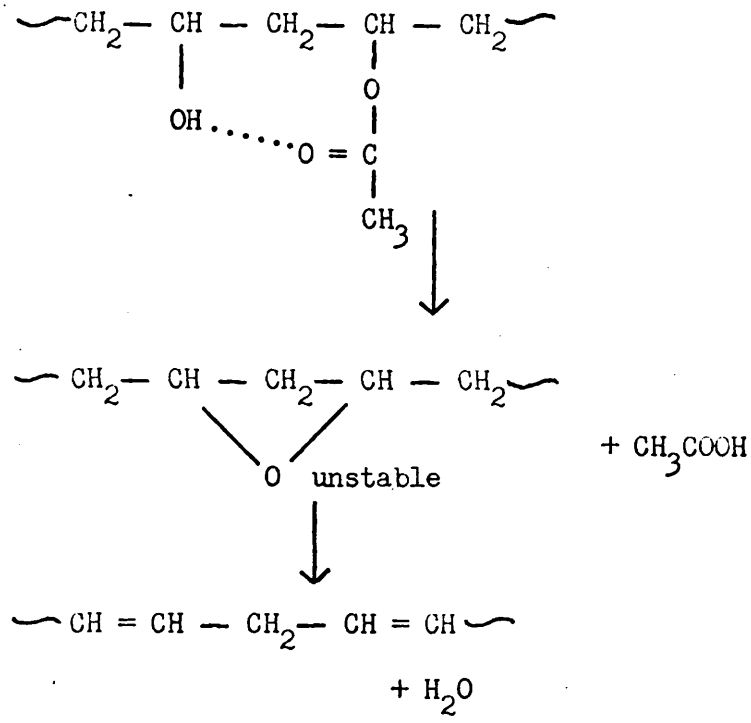


Fig. 4:32 Acetic acid evolution from saponified (—O—), and alcoholysed copolymers (— x —) V-OAc/V-OH, $^{50}/_{50}$.



which could be revealed by the identification of the cyclic ether structure as an intermediate product. Strong i.r. absorption by such a structure should occur in the region 970 - 980 cm^{-1}.

50 mg samples of the copolymer were degraded in steps by programmed heating. Saponified and alcoholysed copolymers of various V-OAc contents seemed to follow a similar course of degradation and therefore a detailed account of only 53·19% saponified copolymer is given in this section.

Fig. 4:33 illustrates the i.r. region of primary interest, in (a) undegraded copolymer, (b) copolymer heated to 367°C at 10°C/min (the first peak max), (c) copolymer heated to 500°C, (d) C.R.F. of the copolymer heated to 500°C. Fig. 4:33(b) shows only the bands of the undegraded 53·19% copolymer except for a new absorption around 3000 cm^{-1}. This new peak is associated with conjugation. The i.r. spectrum of the degradation products of the copolymer degraded to 367°C is shown in Fig. 4:34 (a) and is accounted for by acetic acid, ketene, CO_2 and water. Fig. 4:33 (c) reveals a number of new absorptions. The peaks

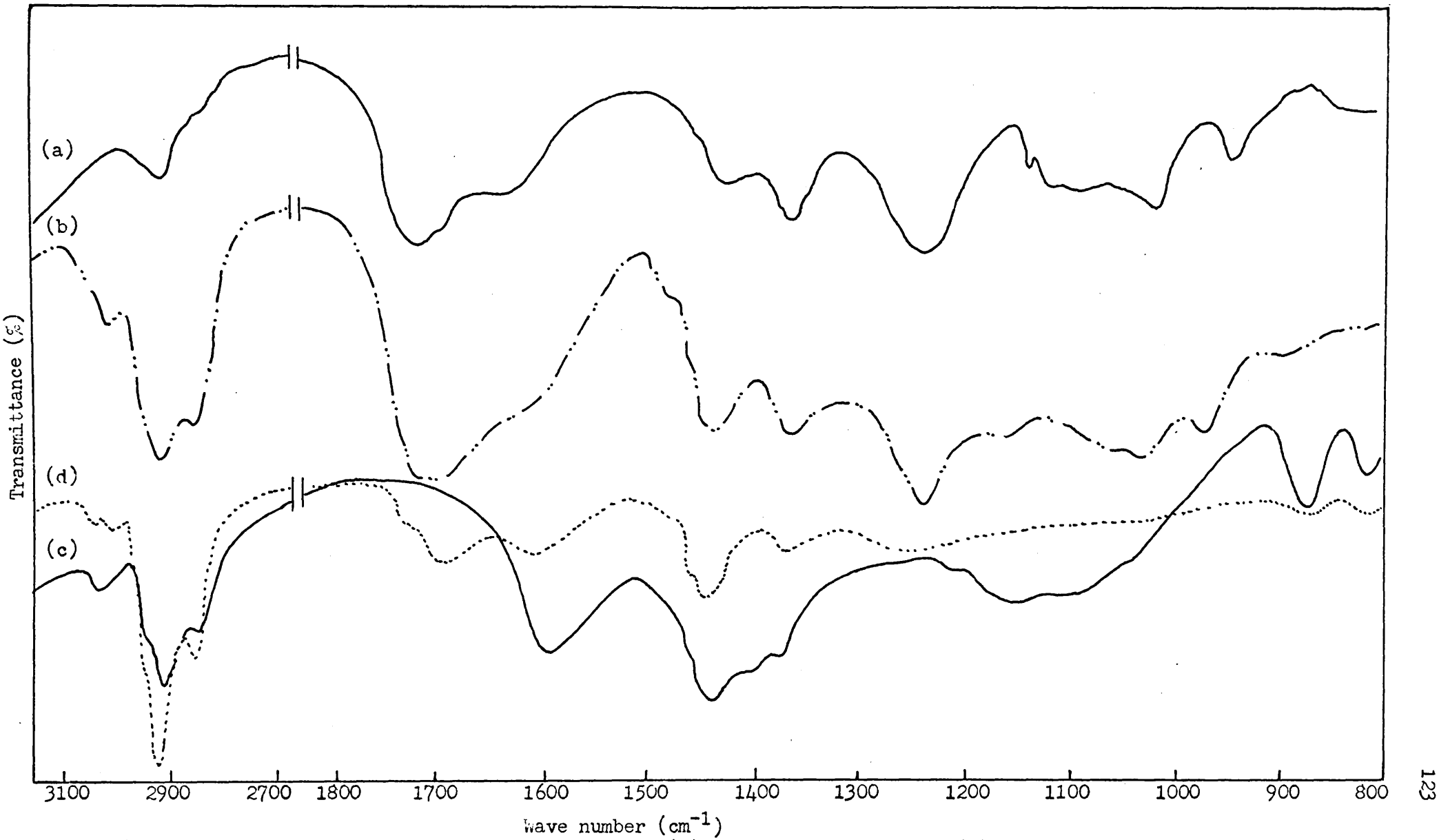


Fig. 4:33 I.R. Spectra of 53.19% saponified copolymer. (a) Undegraded copolymer, (b) copolymer heated to 367°C, (c) copolymer heated to 500°C, (d) C.R.F. of the copolymer heated to 500°C.

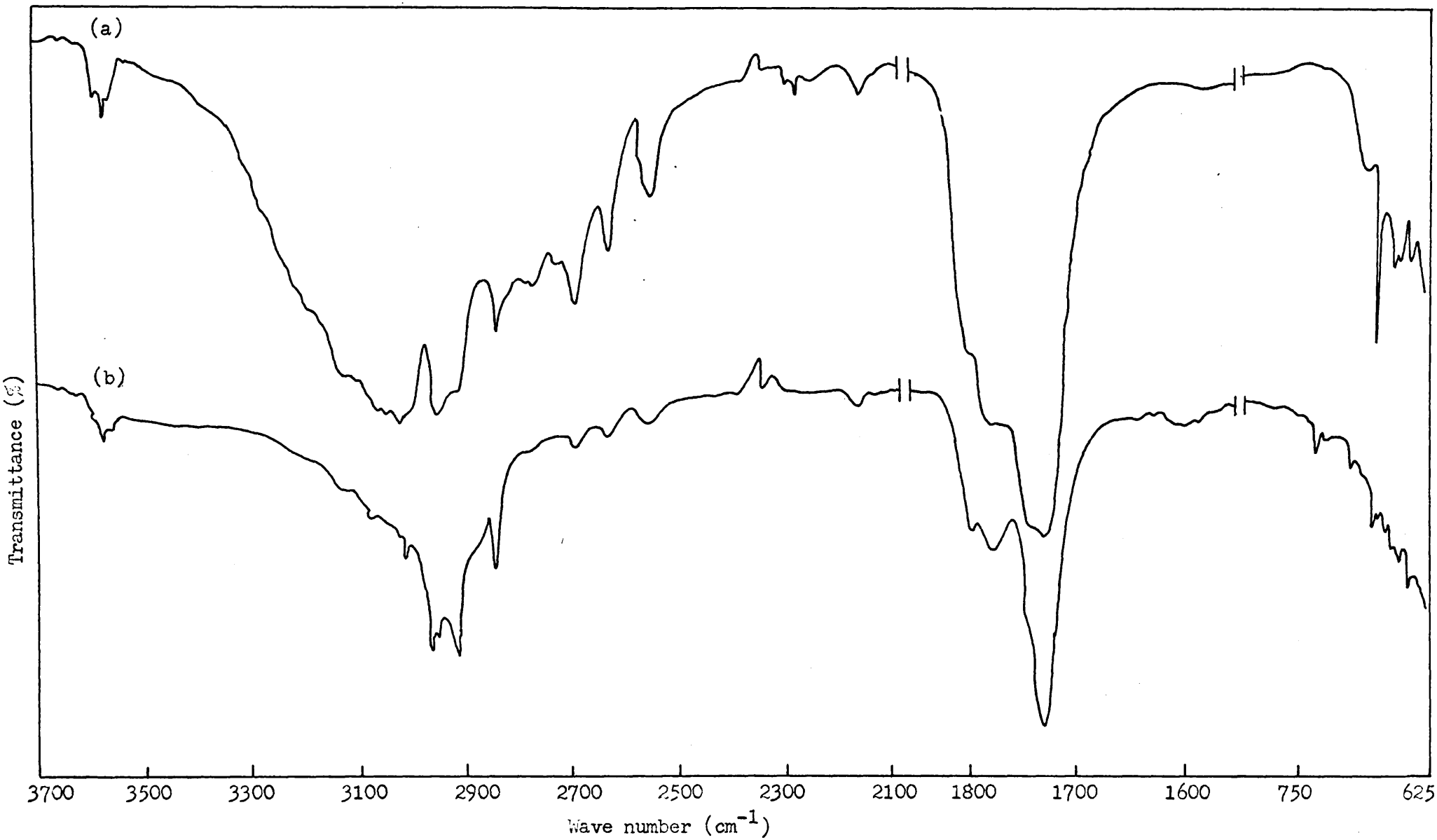


Fig. 4:34 I.R. Spectra of the condensable degradation products of 53.19% saponified copolymer. (a) Copolymer heated to 370°C, (b) copolymer heated from 414°C to 500°C.

above 3000 cm^{-1}, bands around 1600 cm^{-1} and in the 800 - 900 cm^{-1} regions arise from conjugation in the degraded copolymer. The C.R.F. of the copolymer degraded to 500°C (Fig. 4:33(d)) shows similar absorptions in addition to residual V-OAc units in the copolymer. Fig. 4:34 (b) shows the degradation products of the second peak of the degraded copolymer. Unsaturated hydrocarbons and water were identified as degradation products.

There is no positive indication, either in the residue or products, of the formation of intermediate cyclic ether structure although very much more thorough investigation would be necessary to eliminate the possibility completely.

H. Discussion and Proposed Reaction Mechanism.

From the shift in values of the initiation of breakdown towards lower temperatures and the similar shift in vlues of T_{max} with increasing acetate content, it would appear that the acetate units are the weak links in the V-OAc/V-OH copolymer chain.

The fact that ketene is produced from the V-OAc/V-OH copolymer degradation seems to agree with Grassie's hypothesis [27] that ketene is a result of the pyrolysis of acetic acid, since acetic acid is produced in the degradation. The presence of methane and carbon dioxide can also be attributed to the pyrolysis of acetic acid.

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

The thermal decomposition of acetic acid has been investigated by Bamford and Dewar [91] who pyrolysed acetic acid by a flow method in quartz tubes in the temperature range 500 - 900°C. It was suggested that the significant reactions occurring were:-

$$CH_3COOH \longrightarrow CH_2 = C = O + H_2O$$

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

$$2\,CH_2 = C = O \longrightarrow CH_4 + C + 2CO$$

$$2\,CH_2 = C = O \longrightarrow C_2H_4 + 2CO$$

Recently, Scotney [92] has observed decomposition of acetic acid to ketene in silica tubes at temperature as low as 380°C using both vacuum techniques and an argon flow system. Also, at 322°C, during the vacuum degradation of cellulose triacetate Scotney [92], observed the production of ketene which he suggested arose from decomposition of acetic acid. There is no evidence to suggest that the decomposition of acetic acid proceeds by either a free radical or molecular mechanism.

The residual copolymer after degradation is highly coloured, the colour being attributed to conjugated structures which may be described as polyacetylene. It was thought that the detection of benzene (spectroscopically) in the later stages of the reaction (at high temperatures) supported this proposal.

Saponified copolymers (a) have longer sequences of V-OH units and thus fewer V-OH/V-OAc pairs than alcoholysed copolymers (b) (see section 2.D). If there was any interaction between V-OAc and V-OH units during

~ AAA — BBB — AAA — BBB ~ (a)

~ AA — BB — AA — BB — AA — BB ~ (b)

where A, V-OAc unit in the chain

B, V-OH unit in the chain

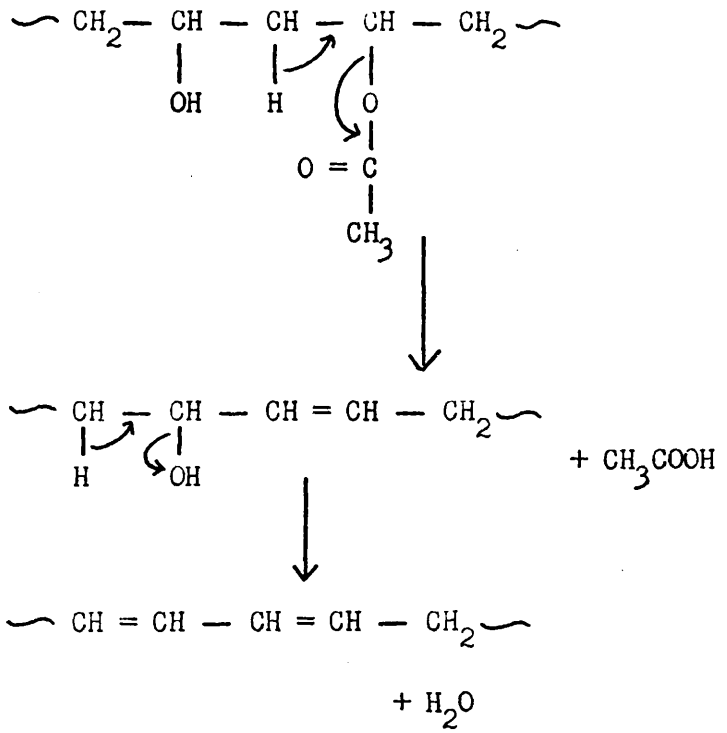
(Both copolymers contain V-OAc/V-OH, 50/50)

degradation in such a way as to initiate degradation, the rate of production of acetic acid would be reported to be higher from (b) than from (a). The higher yield of acetic acid from (a) than from (b)

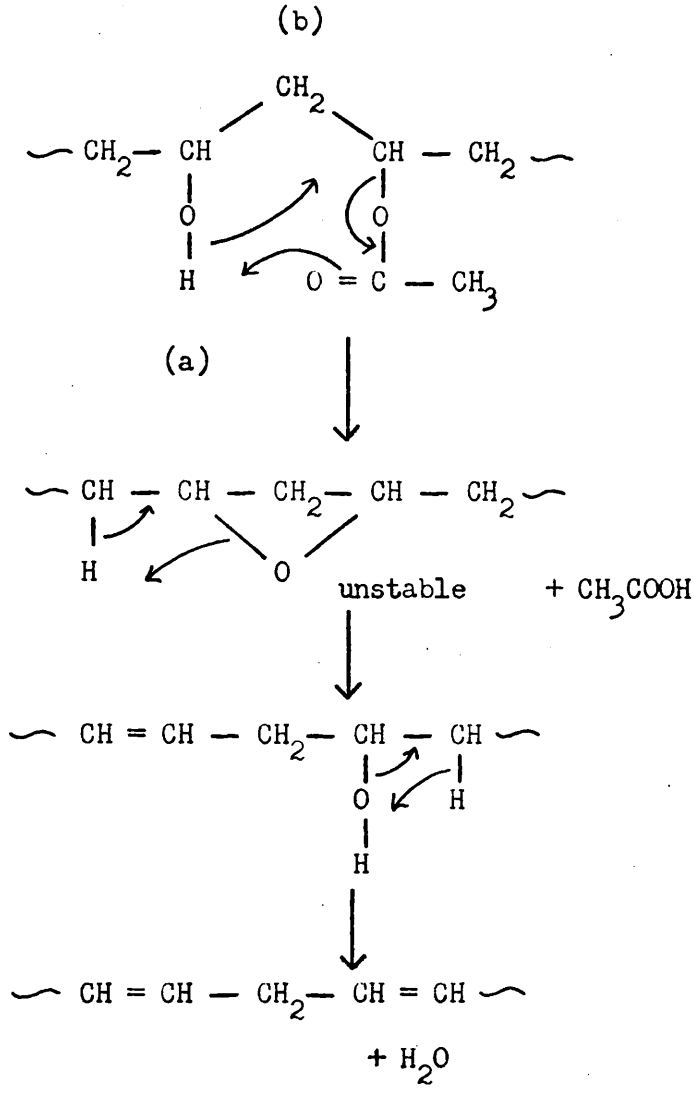
(see Fig. 4:32) suggests that there is no interaction between the two units.

TVA investigations have shown that acetic acid and water are produced in two separate steps during degradation suggesting that the units in the copolymer decompose quite separately.

The following reaction mechanism is suggested to account for the major degradation products evolved from the copolymers.



Since in the copolymer chain, hydrogen (a) is more acidic than hydrogen (b), interaction between acetate and hydroxyl groups seems possible and the following degradation mechanism may thus be suggested.



Acetic acid elimination in the first step of the degradation mechanism leads to the formation of a four membered ring, which was not detected during the examination of degradation products and cold ring fractions of the copolymers. This would appear to rule out the possibility of any interaction between acetate and hydroxyl groups in the copolymer chain in such a way as to initiate degradation but the four membered cyclic ether ring would be fairly unstable and presumably difficult to detect.

3. Summary.

(i) The degradation of PV-OAc results in loss of acetic acid by a chain reaction, which is initiated at random in the polymer molecule by the loss of an acetic acid molecule and the formation of at least one double bond, thus facilitating the elimination of further molecules by allylic activation.

(ii) Madorsky [28] suggests that a radical mechanism is in operation during PV-OAc degradation. This would involve thermal scission of C - O bonds as the initiation step, forming an acetate free radical. Abstraction of hydrogen atoms by acetate free radicals may also take place intermolecularly, resulting in cross-linkages and insolubility of the polymer residue [32]. The consensus of opinion appears to be in favour of a molecular mechanism.

(iii) The formation of volatile products in addition to acetic acid during PV-OAc degradation occurs by decomposition of acetic acid to ketene, water, carbon dioxide and methane, and also by secondary decomposition of ketene itself.

(iv) The subsequent reaction of the polyene sequences at higher temperatures probably occurs by a Diels-Alder type reaction [82,83], leading to aromatic structures.

(v) In the V-OAc/V-OH copolymer system, there is less material evolved than for PV-OAc during deacetylation, which is non-condensable at -196°C and the T_{max} for deacetylation is higher than for PV-OAc, since each short V-OAc sequence requires its own initiation step.

(vi) In the V-OAc/V-OH copolymer system, the stability to weight loss decreases with the increase of V-OAc content in the copolymer.

(vii) The copolymers are less stable than PV-OAc below 340°C but exhibit greater stability at higher temperature.

(viii) The melting temperature (T_m) of the copolymers is not a simple function of the composition, but depends upon the method of preparation of copolymers. This is associated with differences in the degree of blocking in the copolymers and a consequent difference in crystallinity.

(ix) The rate of acetic acid evolution from saponified copolymers is higher than that from alcoholysed copolymer (containing the same V-OAc content) over a range of temperatures.

(x) There is no interaction between V-OAc and V-OH units during degradation of V-OAc/V-OH copolymer and deacetylation of V-OAc units proceeds separately from and at lower temperatures than decomposition of the V-OH units.

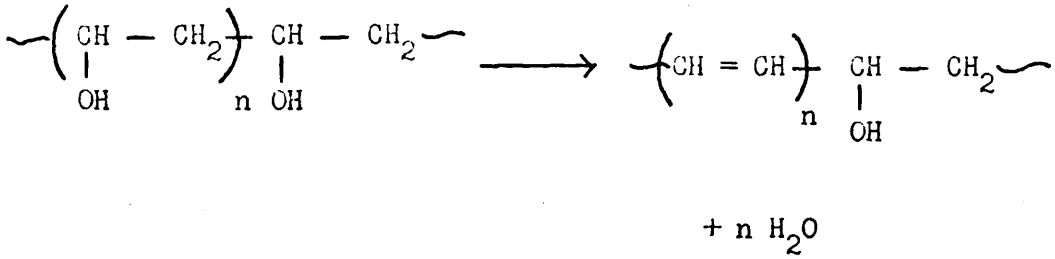
CHAPTER FIVE

THE THERMAL DEGRADATION OF POLY(VINYL ALCOHOL) AND COPOLYMERS OF VINYL ALCOHOL AND VINYL BUTYRAL

1. The Thermal Degradation of Poly(Vinyl Alcohol).

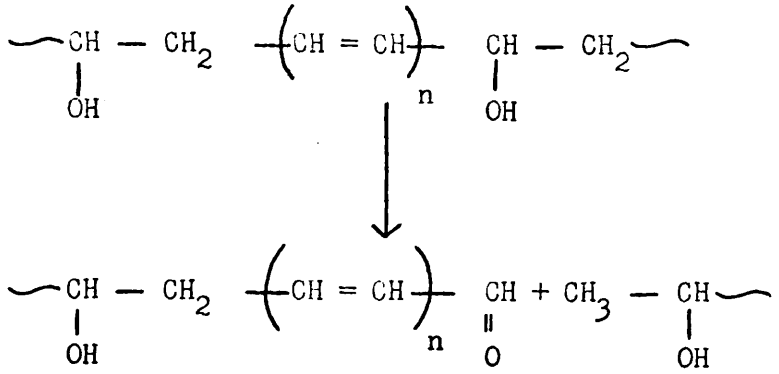
A. Introduction.

A description of previous work on the thermal degradation of PV-OH[25,33-45] has been given in Chapter One. The main products of degradation have been shown to be water from the elimination reaction, and acetaldehyde from depolymerisation. Futama and Tanaka [35] found that the major product, water, was formed principally in two stages, namely, at 90°C and 200°C. The water evolved at 90°C was believed to have been trapped in the polymer matrix and that evolved at 200°C represented true degradation involving dehydration of the polymer chain. Gilbert and Kipling [40] and Tsuchiya and Sumi [43] have deduced that the degradation mechanism of PV-OH is analogous to that of PV-OAc, water being eliminated from the polymer chain, leaving a residual conjugated polyene structure:



$$+ n\ H_2O$$

Scission of carbon-carbon bonds could also result in terminal carbonyl structures.



B. Thermal Volatilisation Analysis.

Fig. 5:1 illustrates the TVA behaviour of PV-OH. An initial low broad peak with T_{max} at 125°C, and not shown in the figure has a -75° curve characteristic of water [66]. Water elimination at this stage is considered to be due to water trapped in the polymer matrix.

The main degradation reaction is associated with the second TVA peak which has a T_{max} at 256°C. Some of the products are trapped at -75°C, some at -100°C and there is a small amount of material non-condensable at -196°C. I.R. spectroscopic analysis shows that they are principally water, acetaldehyde and acetic acid, the first two being eliminated at a lower temperature than the last. Formaldehyde [89] and hydrogen [40] have also been reported and account for the responses after the -100°C and -196°C traps. The remaining two peaks which have T_{max} at 455°C and 512°C respectively, are associated with the breakdown of the polyene structures.

A typical TVA trace of the degradation products from PV-OH is shown in Fig. 5:2. The vertical broken lines indicate the fractions into which the products were separated for i.r. analysis, and the dotted line, the temperature corresponding to the trap from which the condensed gases are progressively volatilising. The gases identified in the four fractions are listed in Table 5.1.

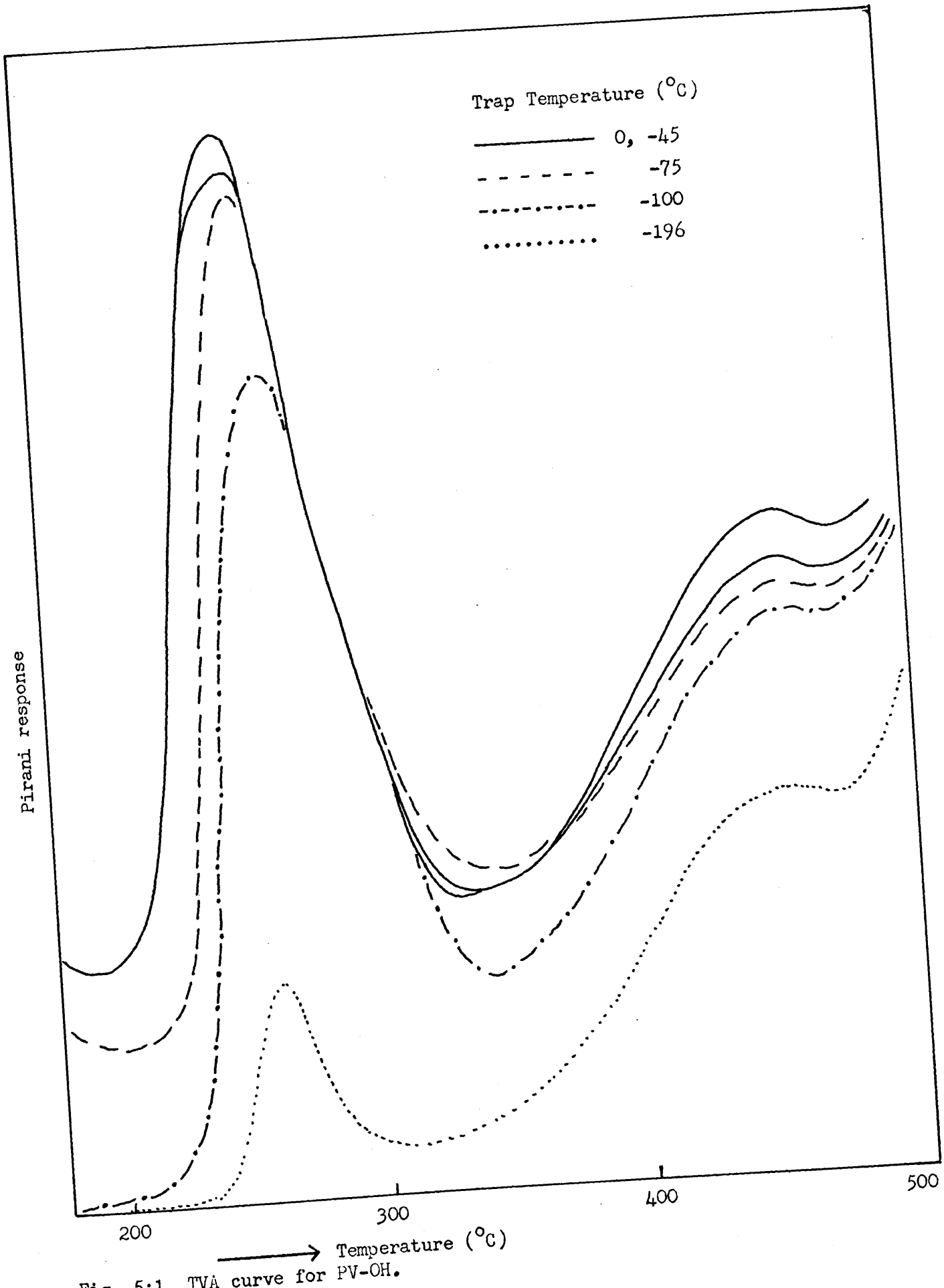


Fig. 5:1 TVA curve for PV-OH.

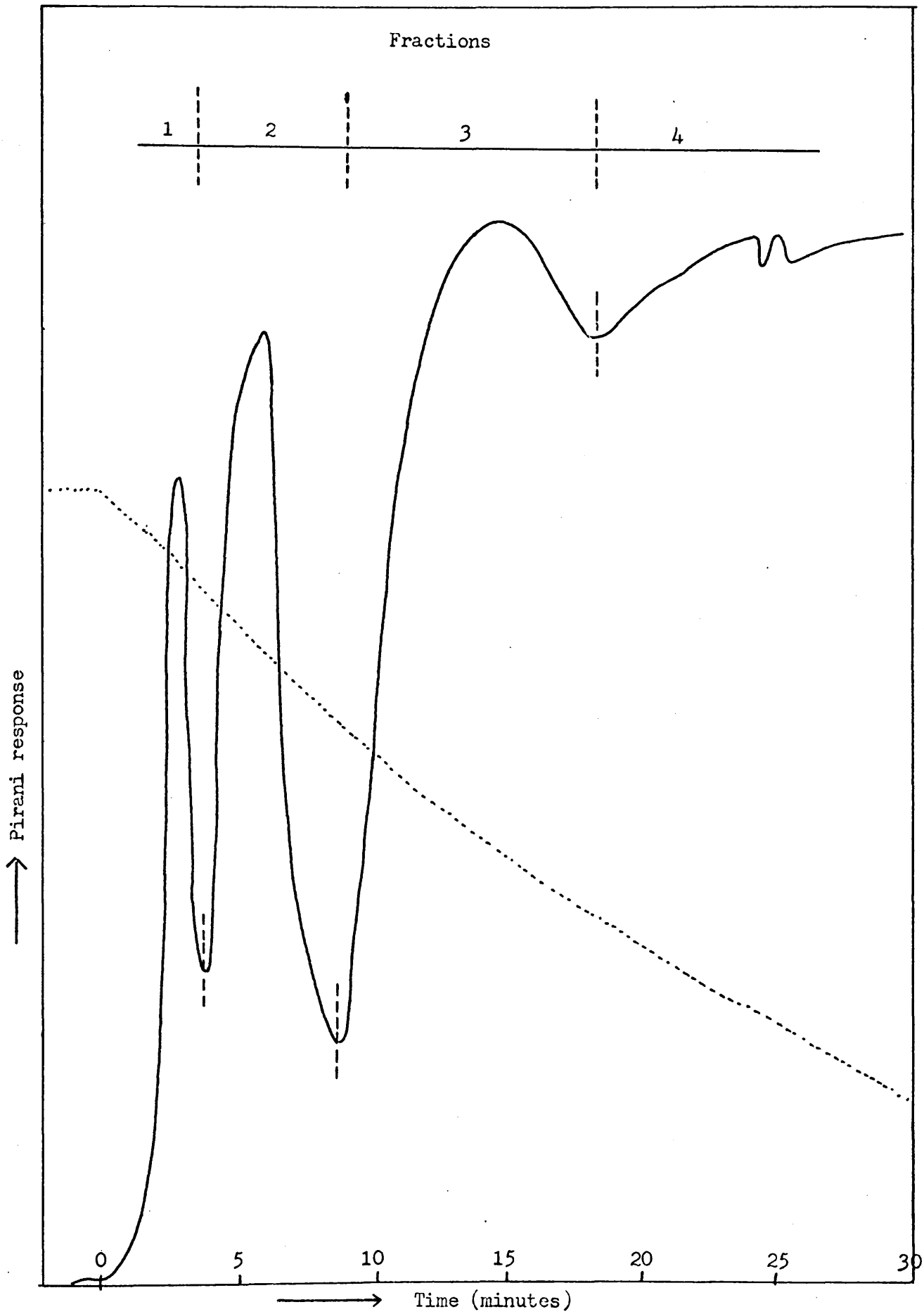


Fig. 5:2 Sub-ambient TVA of condensable gases from degradation of Poly(vinyl alcohol).

Table 5.1.

Gases Produced in TVA of PV-OH.

FRACTIONS			
1	2	3	4
Ethylene	carbon dioxide ketene Isobutene Propylene water	water Acetaldehyde	water

C. Thermal Gravimetric Analysis.

T.G. traces for the two polymers A and B (the polymer B was used for the preparation of copolymers of V-OH and V-B) containing 11-13% and 1·5-2% unhydrolysed V-OAc groups respectively are shown in Fig. 5:3. There are two distinct regions of weight loss leaving 8% and 10% residues at 500°C respectively. The first stage of weight loss is due to elimination of water and acetic acid, the second corresponding to the breakdown of the polyene structures.

Polymer A is more stable than polymer B [93]. Combined figures 5:1 and 5:3 show that the thermal breakdown of the homopolymer B starts and approximately the same temperature under nitrogen and in vacuum.

The loss in weight of the polymer during isothermal heating under nitrogen was investigated at 120, 125, 135 and 150°C. The rate of weight loss increases with the temperature (Fig. 5:4), slowing down as the reaction proceeds. From an Arrhenius plot (Fig. 5:5) of the initial rates a value of 11·0 kCal/mole of the activation energy was calculated.

D. Differential Thermal Analysis. DTA traces for the same two polymers A and B are shown in Fig. 5:6. The endotherm stretching from 100-150°C for the polymer B is associated with the elimination of physically absorbed water. The second endotherms in the region 181-209°C are associated with melting point, the melting point of polymer B being higher due to its higher crystallinity. The endotherms at higher temperature reflect the degradation of the polymer while the exotherms are probably associated with cyclisation processes.

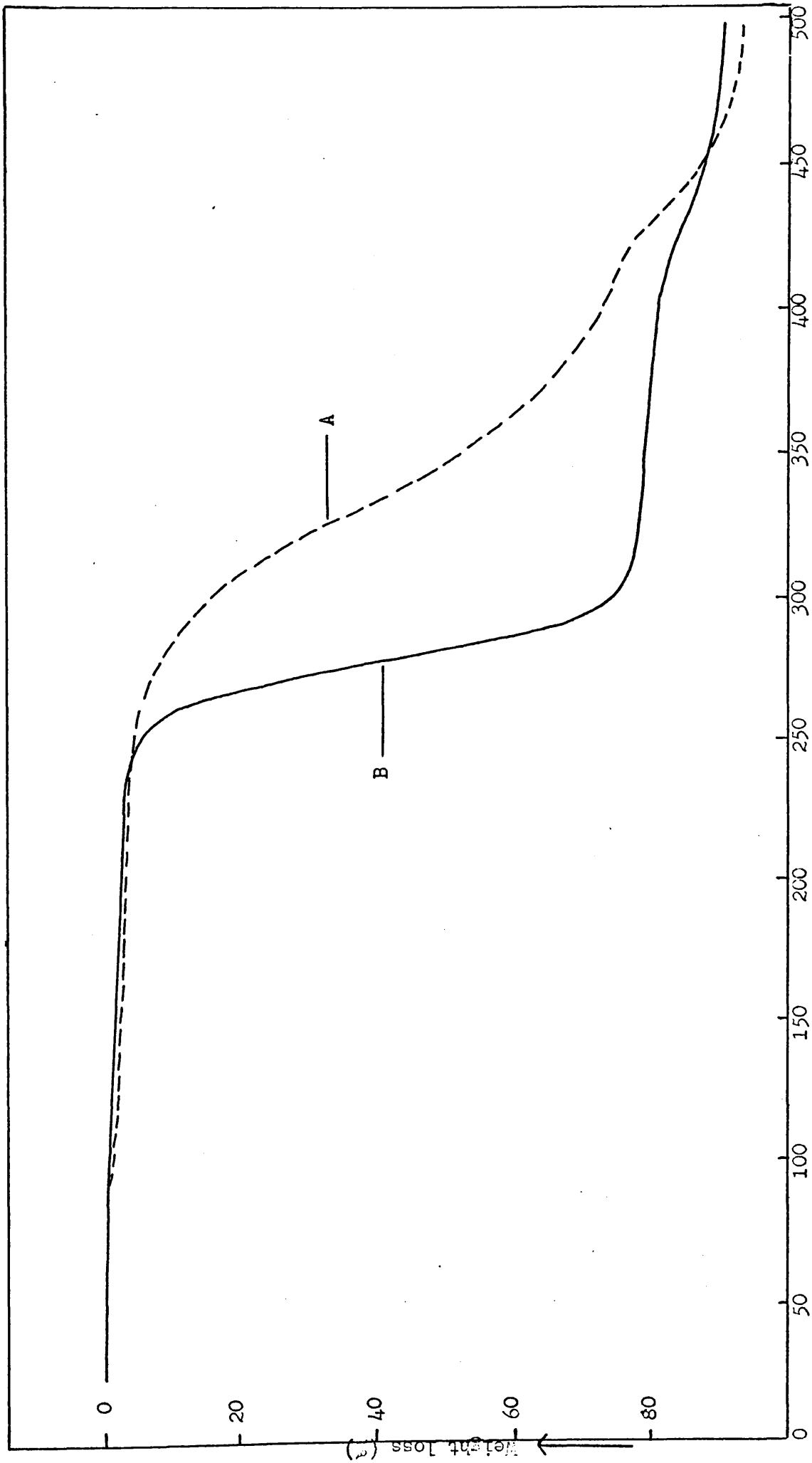


Fig. 5:3 TG curves for Poly(vinyl alcohol), A and B, Dynamic N_2 atmosphere, Heating rate 10°/min.

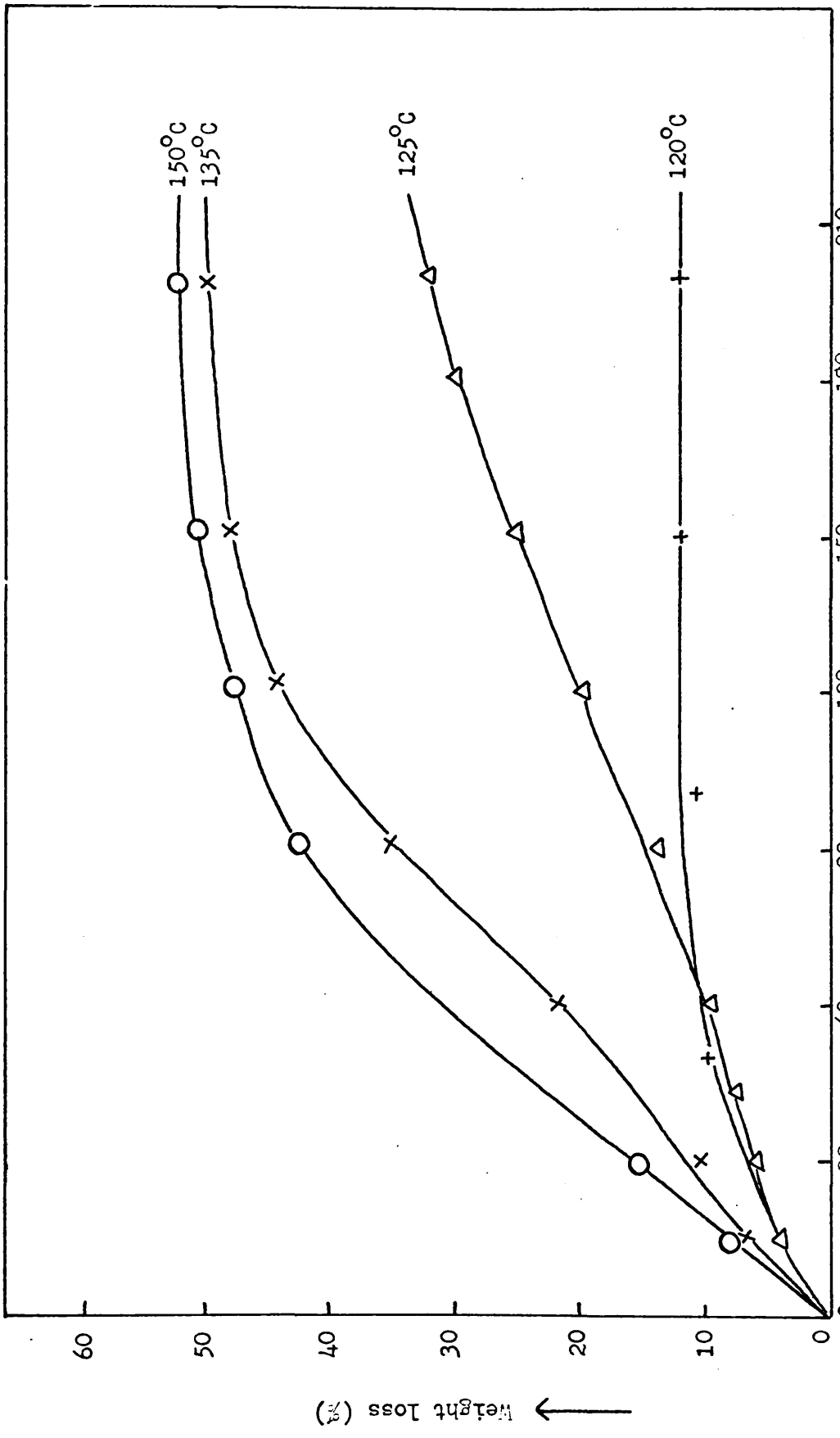


Fig. 5:4 Weight loss of Poly(vinyl alcohol) as a function of time at various temperatures.

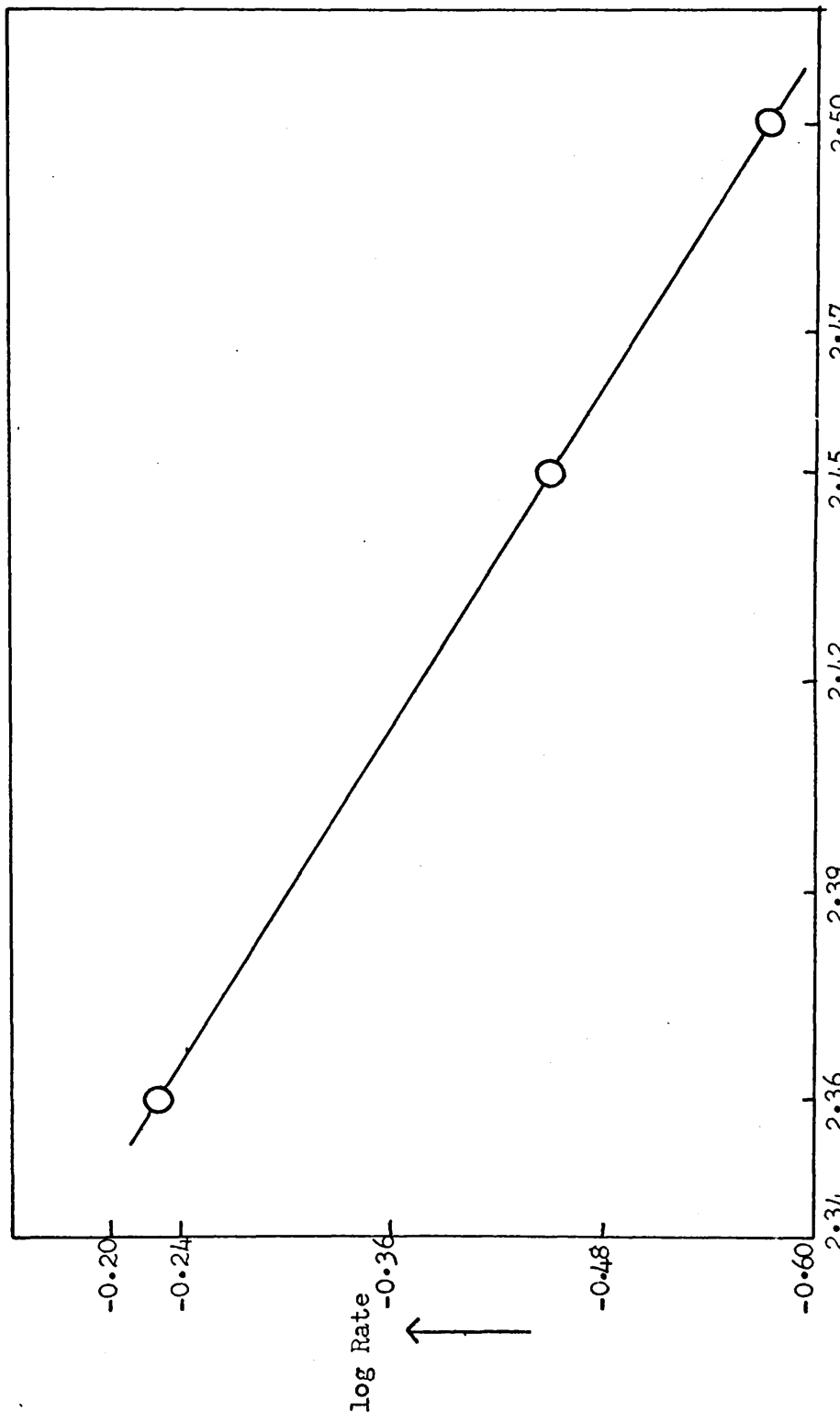


Fig. 5:5 Determination of the energy of activation for PV-OH by plotting values of log Rate versus $^{1}/T\ k^{o}$. (the Arrhenius plot).

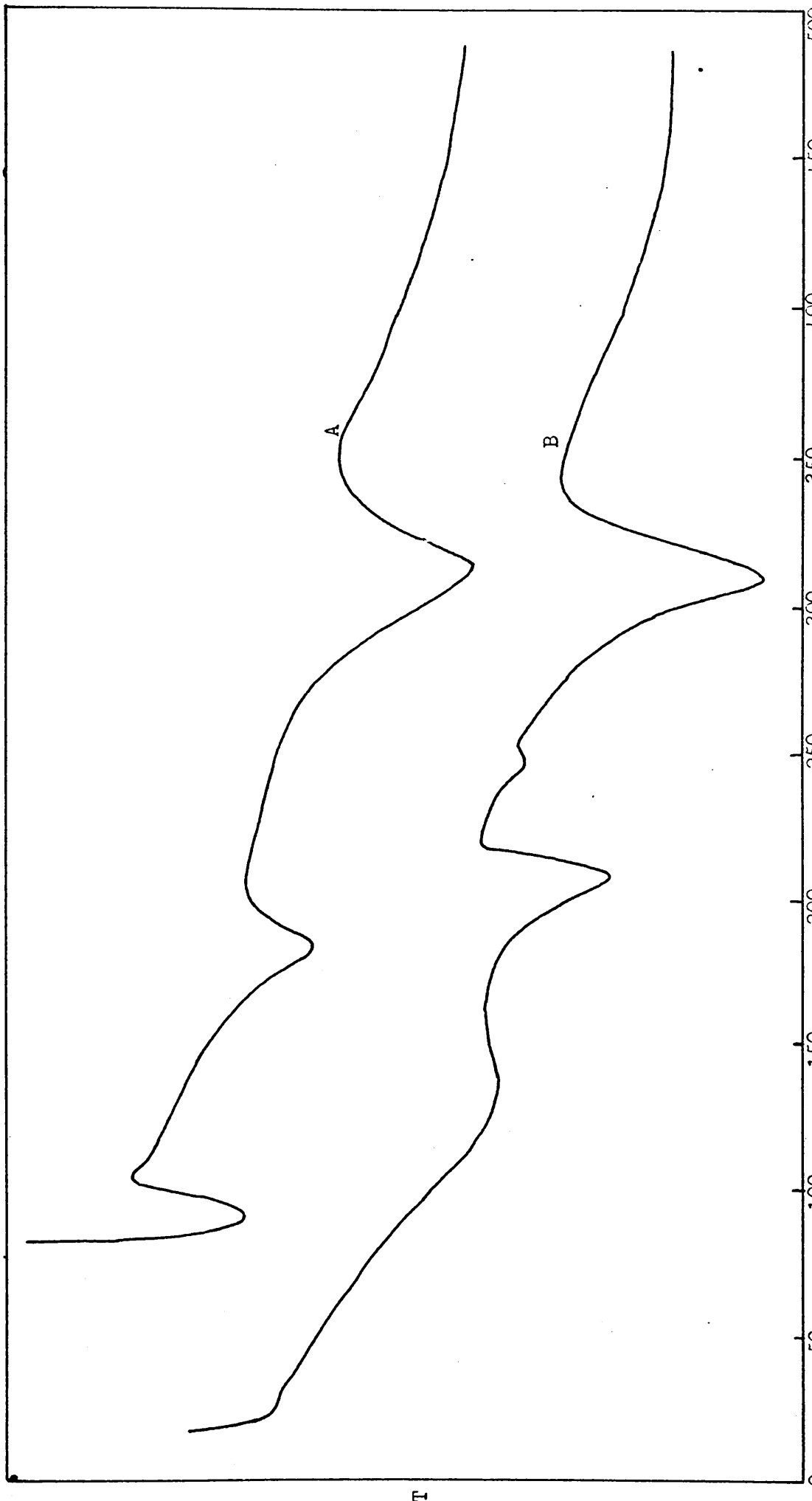


Fig. 5:6 DTA curves for Poly(vinyl alcohol), A and B., Dynamic N_2 atmosphere, Heating rate 10°/min.

E. Product Analysis.

(a) I.R. Analysis of the Volatiles. I.R. spectra of the volatile products of PV-OH degraded in steps are shown in Fig. 5:7.

Fig. 5:7(a) shows the i.r. spectrum of the polymer heated to 150°C. The absorption in the region 3380 - 3460 cm^{-1} is attributed to physically absorbed water. The main degradation products in the region 200 - 325°C (Fig. 5:7(b)) are water and acetaldehyde. The absorptions at 3400 - 3490 cm^{-1} and at 1640 cm^{-1} are associated with water. The absorptions due to C = O of acetaldehyde occur at 1710, 1730 and 1750 cm^{-1}. Some non-condensables formed at this stage might be formaldehyde [89] and hydrogen [40] which could not be observed in the present study. Fig 5:7(c) corresponds to the i.r. spectra of the volatile products of the polymer heated between 325 - 500°C. Absorptions at 2300 - 2320 cm^{-1} and below 700 cm^{-1} are associated with carbon dioxide while those between 700 and 950 cm^{-1} are due to unsaturated hydrocarbons.

These experiments demonstrate that the V-OH and residual V-OAc units decompose separately, the latter units at higher temperature than the former.

(b) I.R. Analysis of the C.R.F. The i.r. spectrum of the C.R.F. obtained from PV-OH after degrading to 500°C is compared with the spectra of the original polymer and residue in Fig. 5:8. Band assignments for the i.r. spectrum of undegraded PV-OH are given in Table 5.2.

The spectrum of the C.R.F. indicates that all carbonyl groups associated with residual acetate groups have been eliminated from the polymer. The peak in the 800 - 900 cm^{-1} regions arise from conjugation in the degraded polymer. The absorption at 1375 cm^{-1} and 1450 cm^{-1} are due to CH_2 bending and $-CH_2-CH_2-$ alkanes

Table 5.2.

Band assignments for I.R. spectrum of PV-OH.

Frequency, cm^{-1}	Intensity	Assignments
3340	Very strong	O-H stretching
2942	Strong	C-H stretching
2910	"	" "
2840	Shoulder	" "
1446	Strong	O-H and C-H bending
1430	"	CH_2 bending
1376	Weak	CH_2 wagging
1326	Medium	C-H and O-H bending
1320	Weak	C-H bending
1235	Weak	C-H wagging
1215	Very Weak	C-C and C-O
1144	Medium	stretching
1096	Strong	C-O stretching and
1087	Shoulder	O-H bending
1040	"	
916	Medium	Skeletal
890	Very Weak	"
850	Medium	"
825	Shoulder	CH_2 rocking
640	broad	O-H twisting
610	Weak	
480	Weak	
410	Weak	

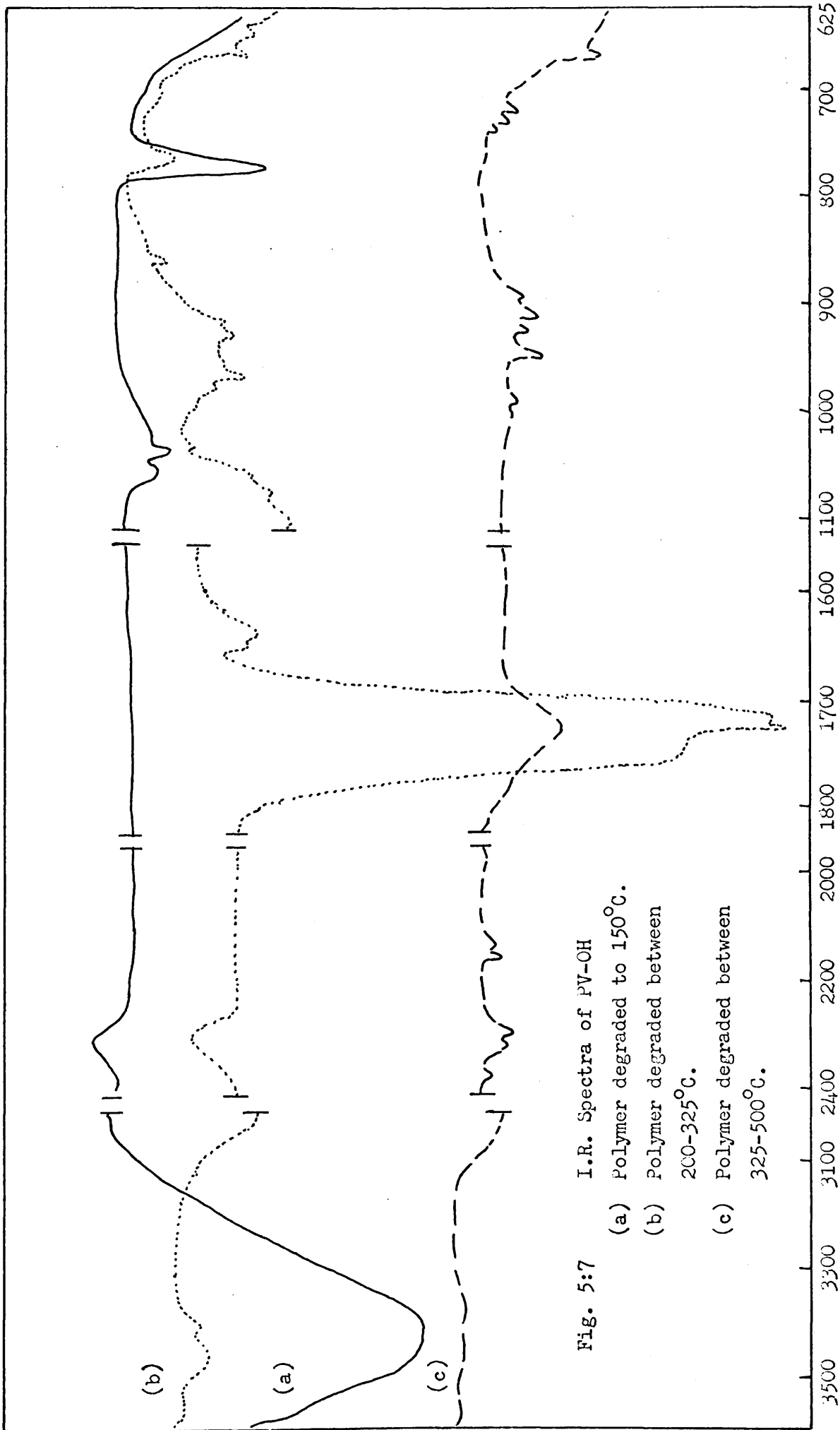


Fig. 5:7 I.R. Spectra of PV-OH

(a) Polymer degraded to 150°C.

(b) Polymer degraded between 200-325°C.

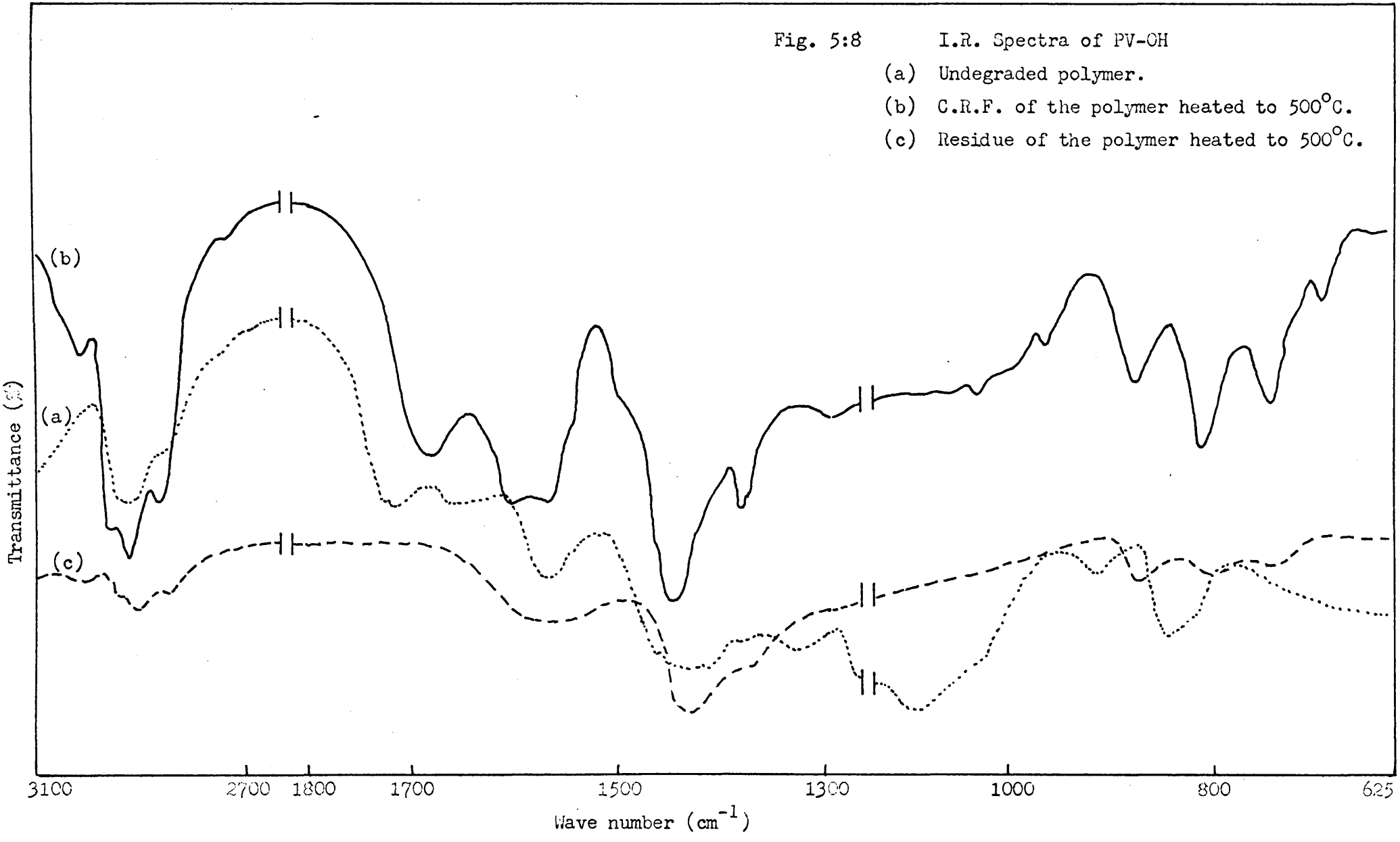
(c) Polymer degraded between 325-500°C.

Fig. 5:8 I.R. Spectra of PV-OH

(a) Undegraded polymer.

(b) C.R.F. of the polymer heated to 500°C.

(c) Residue of the polymer heated to 500°C.

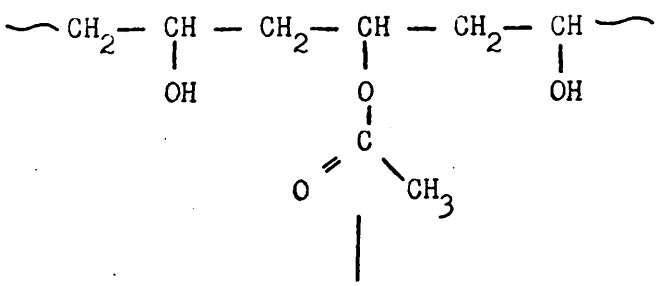


respectively. The absorptions in the 2840 - 2950 cm^{-1} regions are attributed to C - H stretching.

(c) I.R. Analysis of the Residue. The main peaks observed in the spectrum of the black residue were as follows,

3020 cm^{-1}	— C = C —
2840, 2920 cm^{-1}	C — H stretching
1550 - 1600 cm^{-1}	— C = C —
1430 - 1440 cm^{-1}	CH_2 bending
1375 cm^{-1}	— CH_2— CH_2 alkanes
810 cm^{-1}	C — H olefinic
880 cm^{-1}	C — H olefinic

There is no hydroxyl absorption indicating that it must therefore be composed of long conjugated sequences resulting from complete elimination of water and the residual 1·5-2% V-OAc units in the chain.



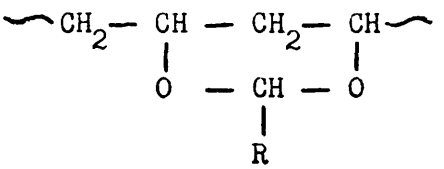
$$+ H_2O + CH_3COOH$$

2. The Thermal Degradation of Copolymer of Vinyl Alcohol and Vinyl Butyral.

A. Introduction.

A description of previous work on the oxidative degradation of copolymer of V-OH and V-B [47-58, 24] has been given in Chapter One.

Comparative investigations of photo and thermal aging of several poly(vinyl alcohol)acetals was made by Popova and Schuvalova [49] using i.r. spectroscopy. These materials of course incorporate unchanged V-OH units in addition to the acetal groups:



The thermal aging of the first member of this series, poly(vinyl formal), (PVF), (R=H), was studied by Beachell, Fotis and Hucks [47]. Two other members of the series, namely, poly(vinyl ethylal), ($R=CH_3$), and poly(vinyl butyral), ($R=C_3H_7$) were also studied [49]. They showed a decrease of the content of OH, CH and C—O— groups together with a build up of C=O groups. Similar work was carried out by O.M. Klimova and co-workers [57] and V.I. Grachev [58] to study the characteristic features of the oxidative degradation of butyrals and copolymers. They found that the rate of formation of polyene systems and carbonyls in the PVB greatly depended upon the content of the butyral groups and the reaction temperature.

It should be noted that i.r. spectroscopy, in addition to substantiating quantitatively the mechanism proposed for the oxidation of acetals by Beachell et. al. [47], indicates that there is a substantial difference between the processes of photo and thermal aging and it is necessary to consider different mechanism for the

decomposition of the acetals of poly vinyl alcohol in different type of aging. In the present study an effort has been made to contribute to the solution of these problems by investigating the composition of the volatile products from the decomposition of copolymers of V-OH and VB degraded in steps under high vacuum conditions.

B. Thermal Volatilisation Analysis.

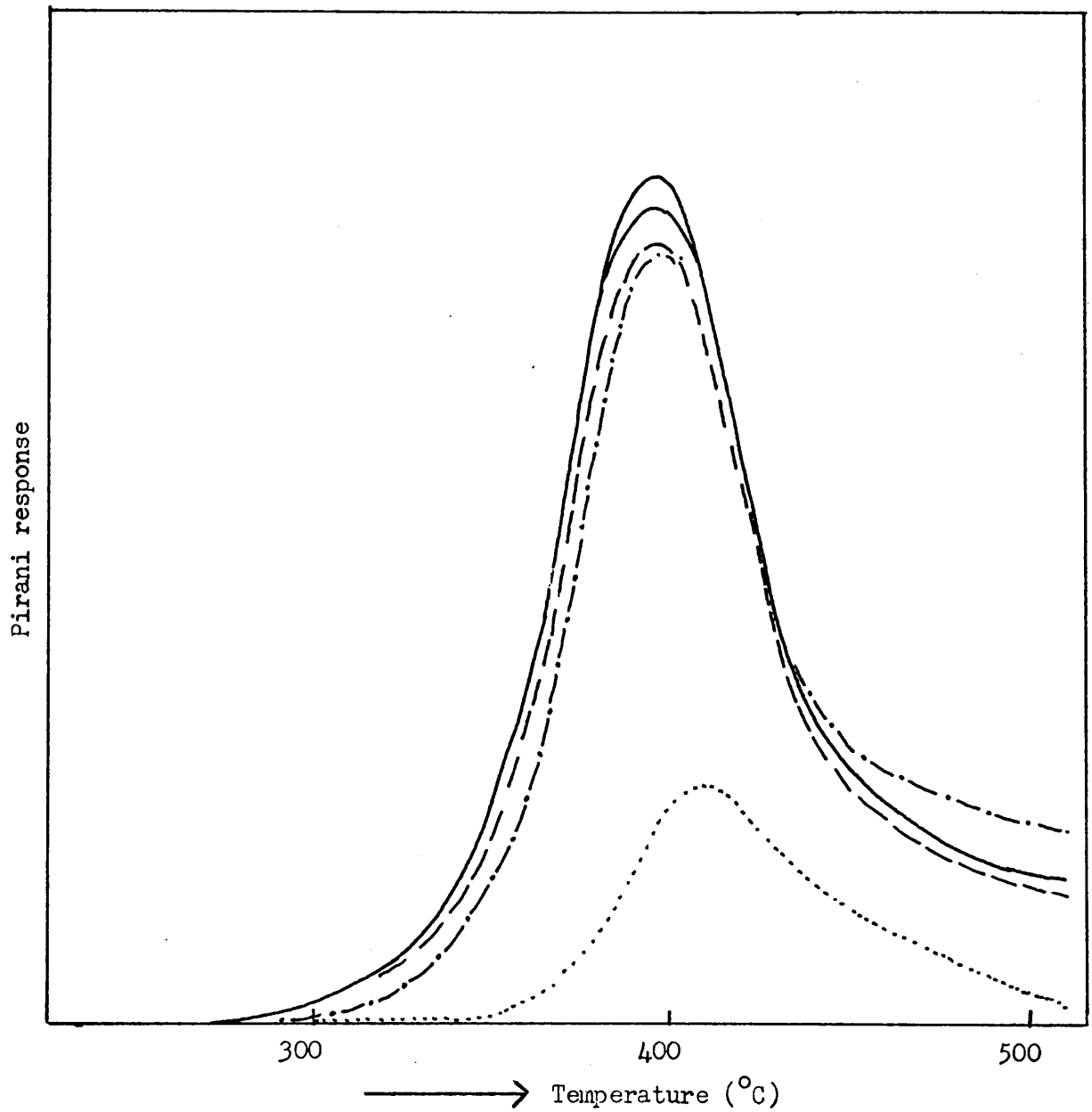
TVA traces for four V-OH/VB copolymers containing 4·75%, 8·68%, 27·47% and 50·9% vinyl butyral are reproduced in Figs. 5:9, 5:10, 5:11 and 5:12 respectively.

The first low broad peak in the region 90 - 160°C not shown in the first three figures is due to elimination of physically absorbed water.

The second peak (much suppressed as compared with PV-OH) appears in the same temperature region as in the case of PV-OH (Fig. 5:1). Analysis of the degradation products associated with this peak stretching between 200 - 300°C indicates that they are acetic acid, water, ketene, carbon dioxide and unsaturated hydrocarbons. This peak is absent in the 4·75% copolymer (Fig. 5:9).

The main degradation reaction is associated with the third peak. The Pirani responses at this peak are mainly due to butyraldehyde, water and acetaldehyde although some more volatile products are also trapped at -100°C and -196°C.

The copolymers are more stable than PV-OH (see section 2. C). The greater stability of the copolymers containing 4·75% and 8·68% VB as compared with PV-OH may be due to the reaction being blocked by VB units which means that each sequence of V-OH requires its own initiation step. The copolymers become less stable with increasing content of VB units in the chain. This may be due to steric interaction of butyral groups.



Trap Temperature °C

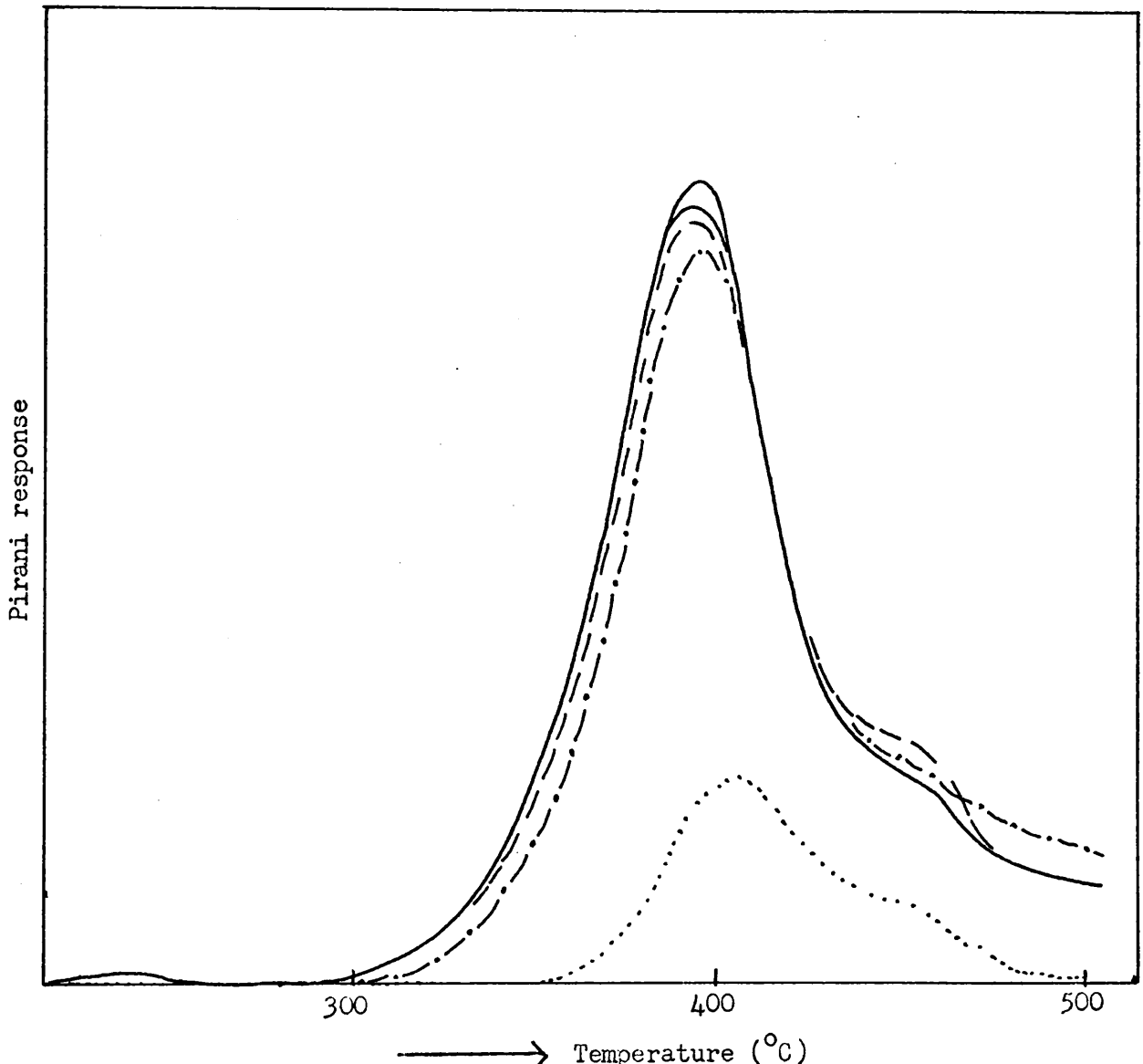
———— 0, -45

- - - - - - -75

-·-·-·-·-·- -100

..... -196

Fig. 5:9 TVA curve for 4·75% V-OH/VB copolymer.



Trap Temperature °C

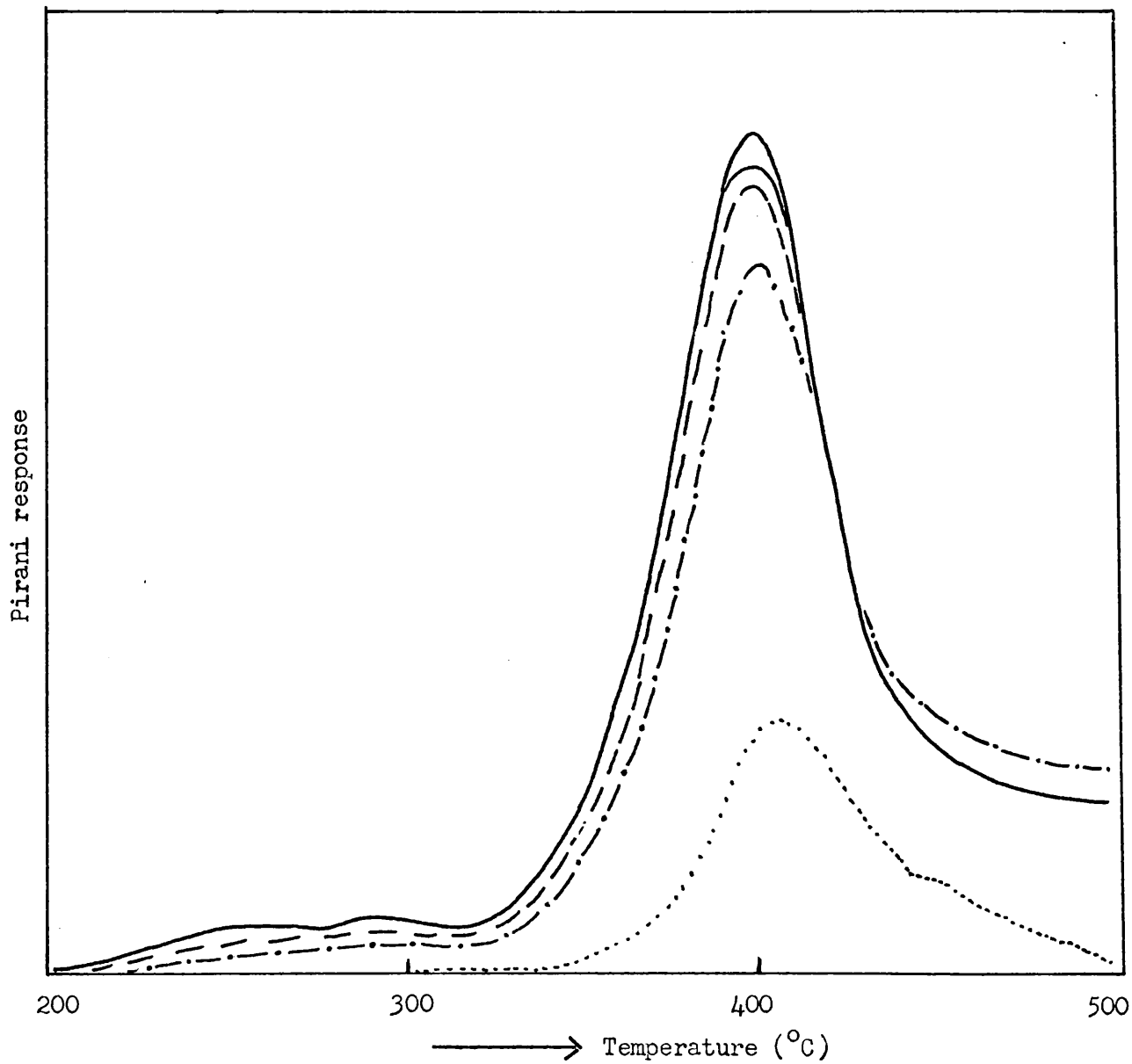
———— 0, -45

- - - - - - -75

-.-.-.-.-.- -100

..... -196

Fig. 5:10 TVA curve for 8·68% V-OH/VB copolymer.



Trap Temperature °C

——————— 0, -45

- - - - - - -75

-.-.-.-.-.- -100

..... -196

Fig. 5:11 TVA curve for 27·47% V-OH/VB copolymer.

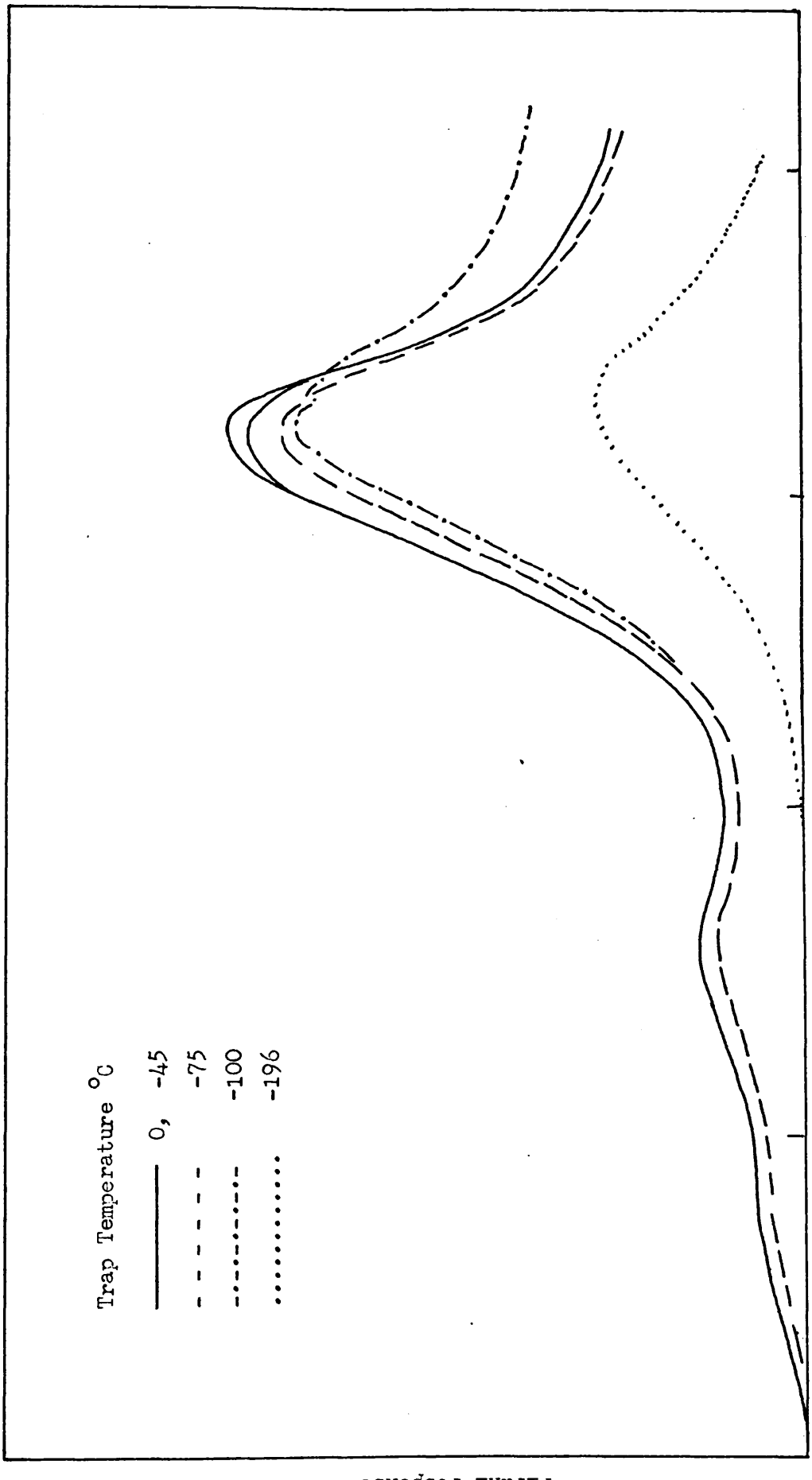


Fig. 5:12 TVA curve for 50.9% V-OH/VB copolymer.

A sub-ambient TVA trace (solid line) of 50·9% V-OH/VB copolymer is shown in Fig. 5:13. The vertical broken lines indicate the fractions isolated for i.r. analysis, and the dotted line the temperature profile of the trap from which the condensable gases are progressively volatilising.

Table 5.3. shows the products identified in each stage of the reaction.

C. Thermal Gravimetric Analysis.

Figs. 5:14 and 5:15 show TG curves for V-OH/VB copolymers containing 0·35%, 1·66%, 4·75% and 4·75%, 8·68%, 27·47%, 49·20% VB respectively.

There are two distinct regions of weight loss. The first stage is associated with the breakdown of V-OAc and V-OH units. The second stage is due to the breakdown of butyral units in the chain.

Weight loss in the alcohol rich polymers at lower temperatures is considered to be the result of the elimination of physically absorbed water. The yield of residue from copolymers (Fig. 5:14) at 500°C does not differ significantly, but it decreases markedly in copolymers (Fig. 5:15) from that formed in the decomposition of PV-OH.

Fig. 5:14 shows that the stability compared with PV-OH is increased greatly by small amounts of butyral units. As in the case of the TVA data described above this is probably due to the butyral units blocking the progress of water elimination from groups of adjacent alcohol units.

Fig. 5:15 demonstrates that the stability to weight loss decreases as the concentration of butyral units is further increased probably due to the electrostatic interaction of the butyral units in the chain.

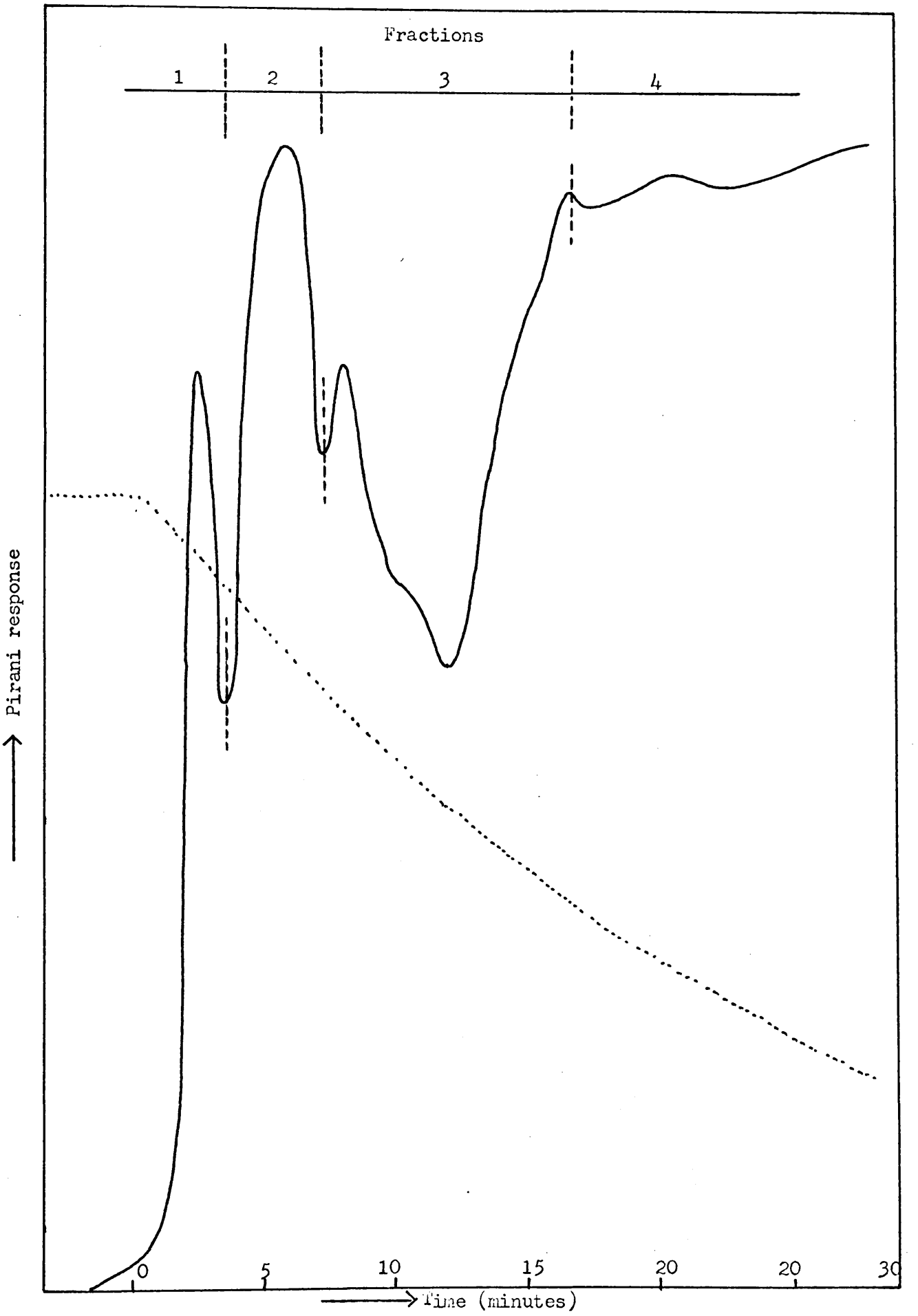


Fig. 5:13 Sub-ambient TVA of condensable gases from degradation of 50·90% V-OH/VB copolymer.

Table 5.3.

Gases Produced in TVA of 50·9% V-OH/VB copolymer.

FRACTIONS			
1	2	3	4
Ethylene Propylene Isobutene	carbon dioxide ketene Propylene Isobutene	water acetaldehyde Butyraldehyde	water

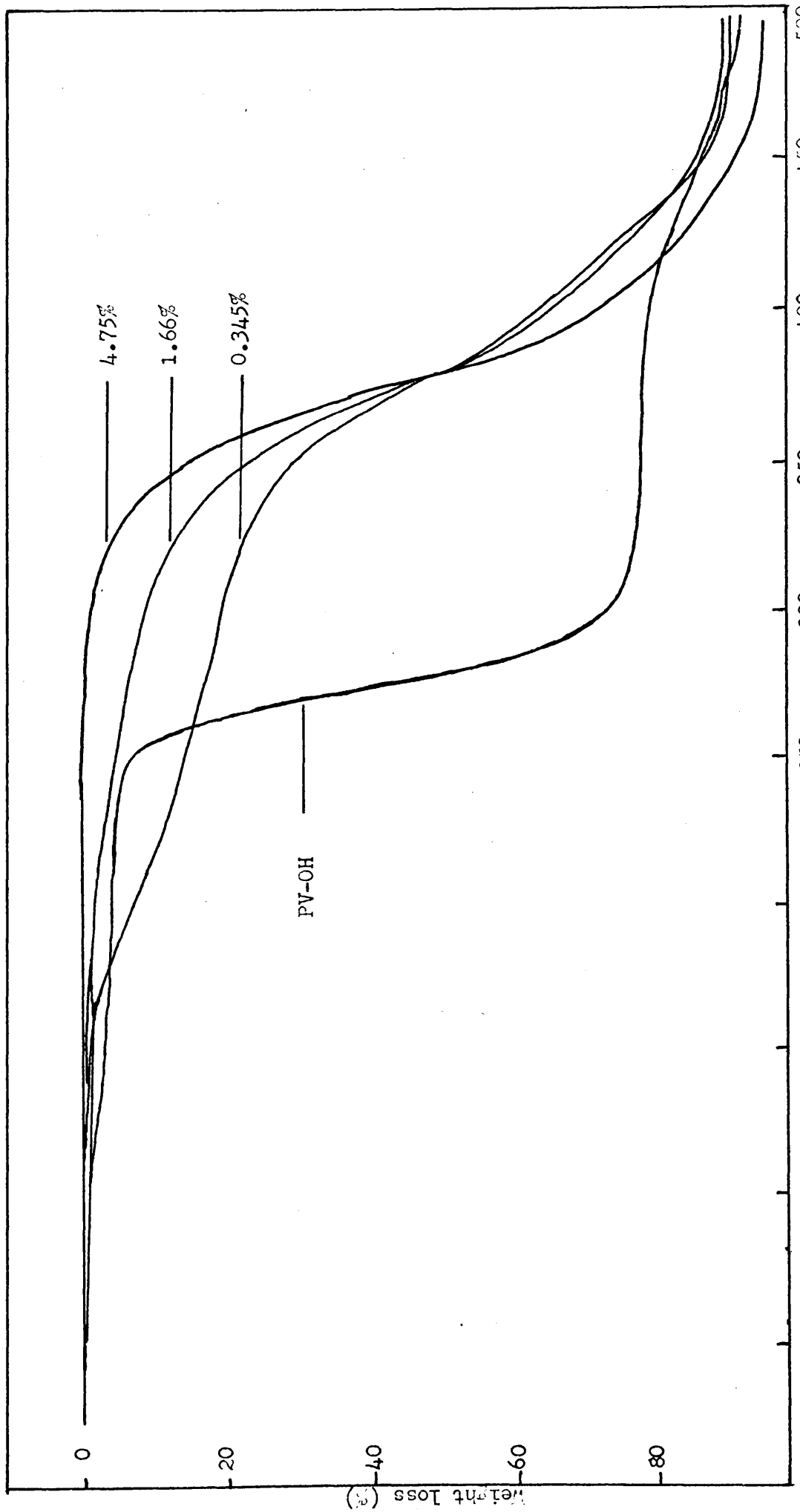


Fig. 5:14 TG curves for V-OH/VB copolymers, Dynamic N_2 atomophere, Heating rate 10°/min.

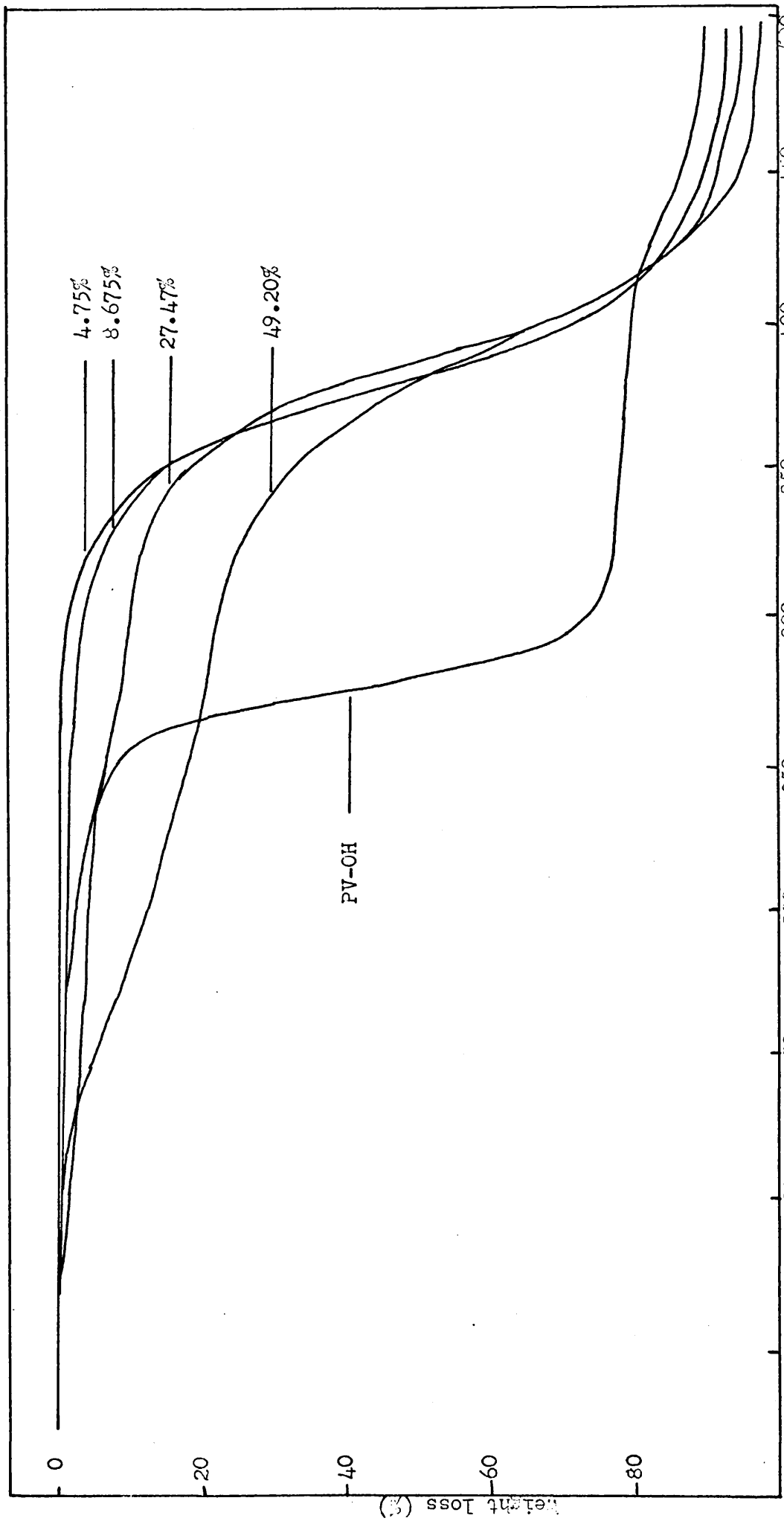


Fig. 5:15 TG curves for V-OH/VB copolymers, Dynamic N_2 atmosphere, Heating 10^{o}/min.

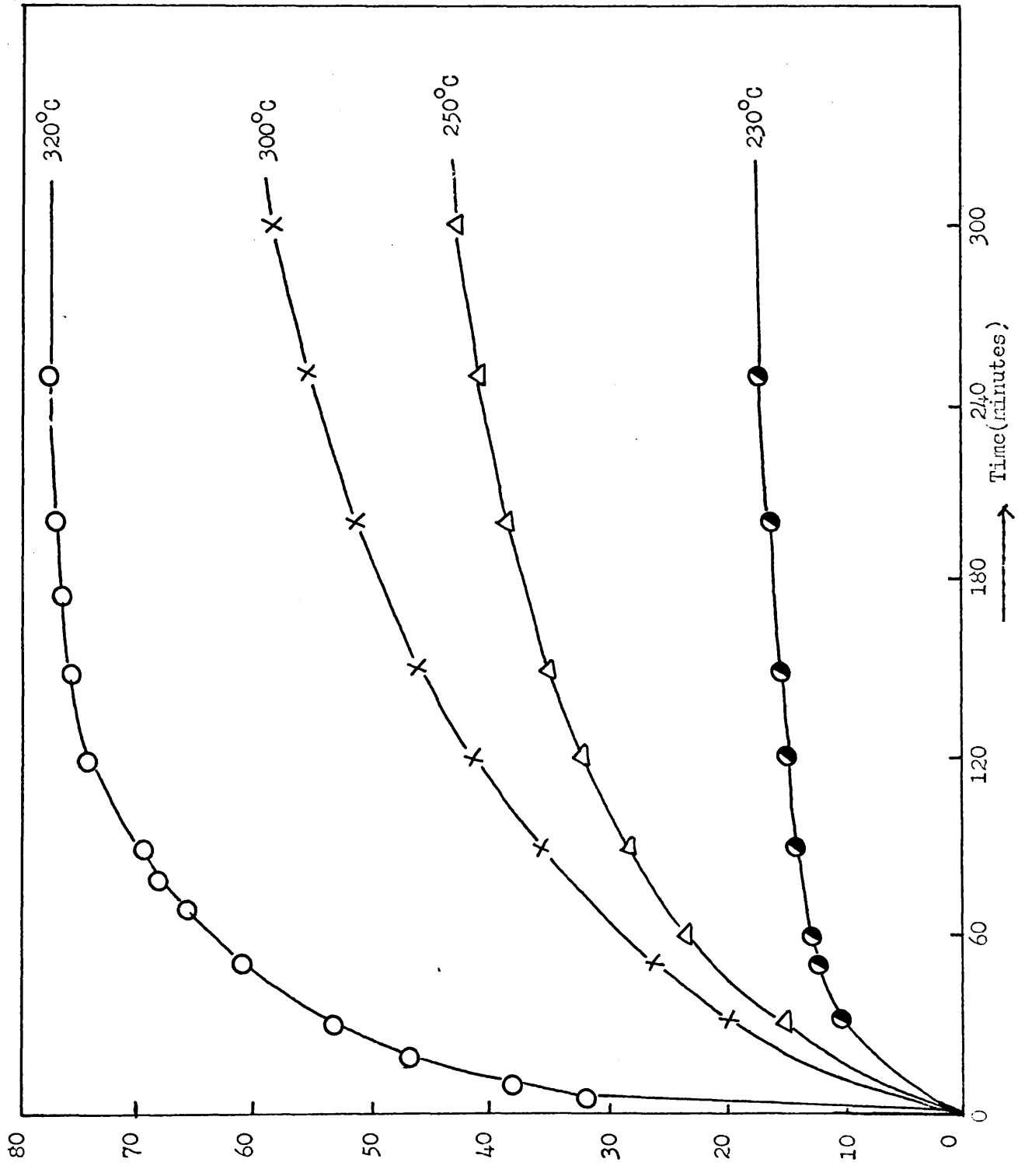


Fig. 5:16 Weight loss of 27.47% V-CH/VB copolymer as a function of time at various temperatures.

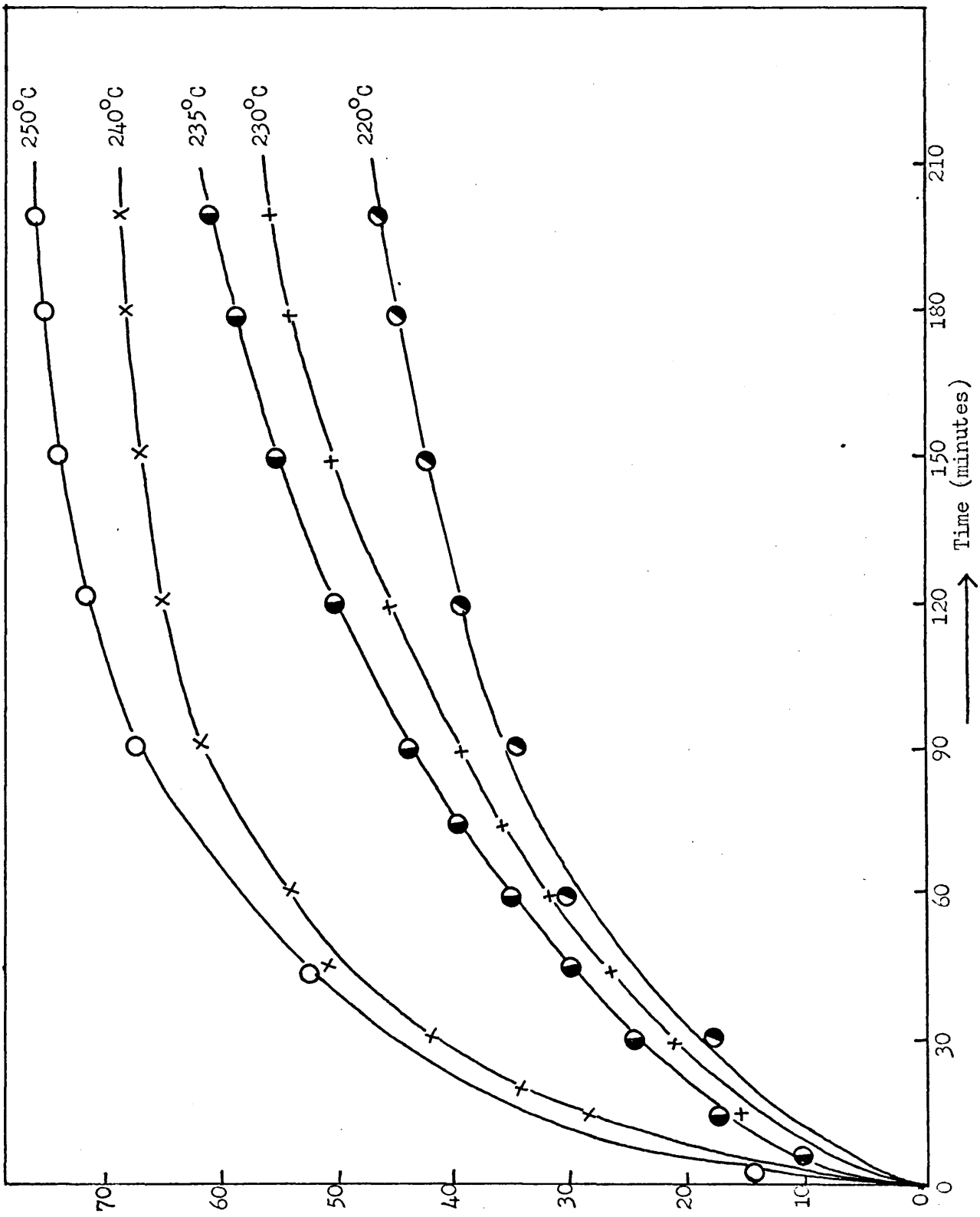


Fig. 5:17 Weight loss of 50.90% V-OH/VB copolymer as a function of time at various temperatures.

The loss in weight of 27·47% and 50·9% copolymers which occurs during isothermal heating under nitrogen was investigated over a range of temperatures and the results are shown in Figs. 5:16 and 5:17 respectively. The latter copolymer is less stable than the former presumably due to greater electrostatic interaction between butyral groups.

D. Product Analysis.

(a) I.R. Analysis of the Volatiles. I.R. spectra of the volatile products obtained from the degradation of 27·47% and 50·9% V-OH/VB copolymers are shown in Fig. 5:18. The i.r. spectra are almost identical differing only in the relative amounts of individual products.

Absorptions at 2300 - 2330 cm^{-1}, 720 cm^{-1} and below 700 cm^{-1} are attributed to carbon dioxide, ketene is identified at 2120 - 2130 cm^{-1}. Absorption by acetic acid (vapour), acetaldehyde and butyraldehyde occurs at 1740 cm^{-1} while those in the range 700 - 950 cm^{-1} are due to unsaturated hydrocarbons and at 3480 cm^{-1} due to water. The appearance of ketene, carbon dioxide are associated with the decomposition of acetic acid.

(b) I.R. Analysis of the C.R.F. I.R. spectra of the C.R.F. obtained from the same copolymers after degradation to 500°C are compared with that of the original undegraded 50·9% V-OH/VB copolymer in Fig. 5:19.

The main peaks observed were as follows,

3020 cm^{-1}	— C = C —
2840, 2920 cm^{-1}	C — H stretching
1400 - 1440 cm^{-1}	V - OH structure
900, 970 - 1000, 1050	
1100 - 1440, 1340, 1380 cm^{-1}	cyclic acetal structure.

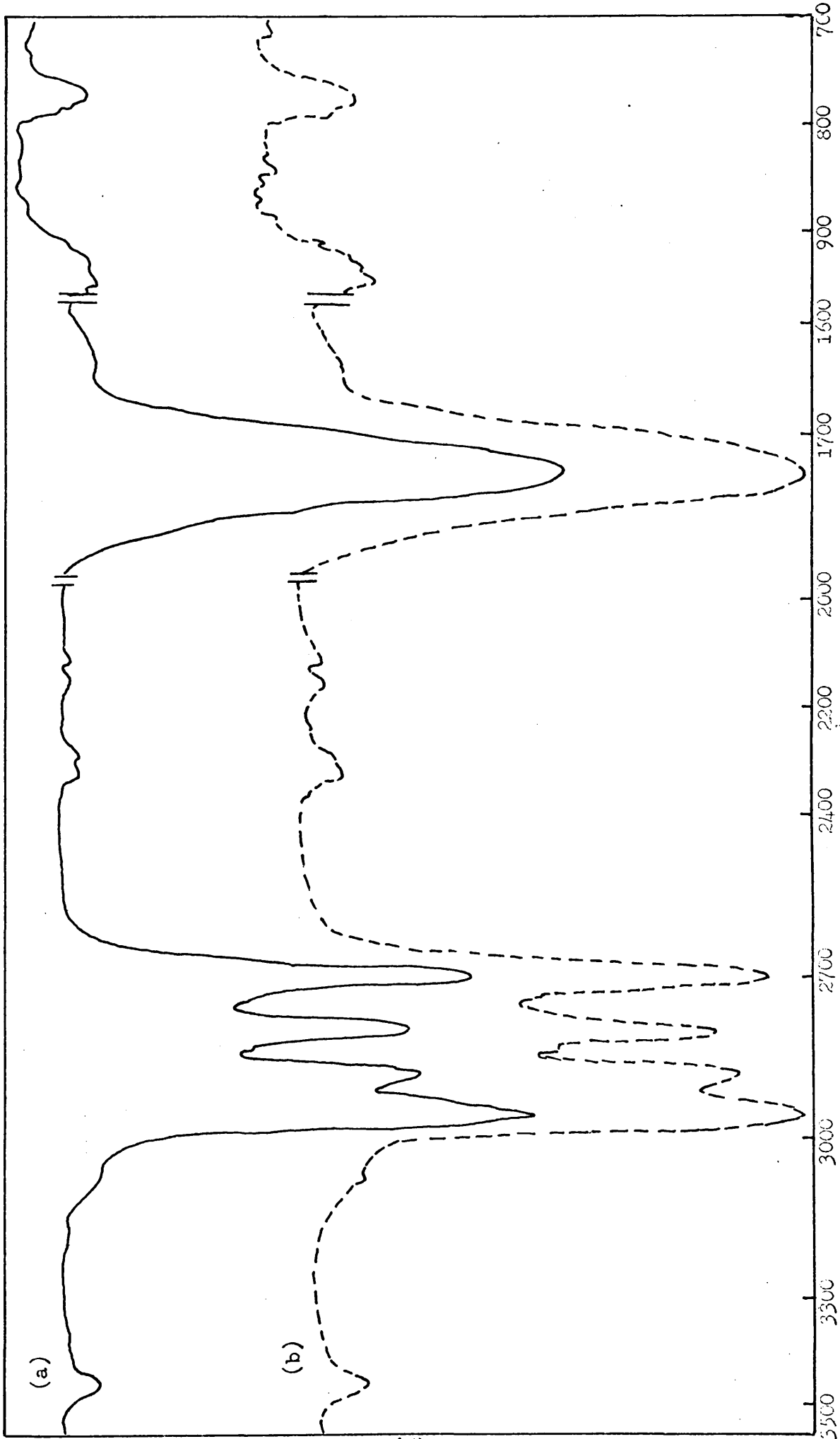


Fig. 5:18 I.R. Spectra of condensable degradation products. (a) 27.47% V-OH/VB copolymer degraded to 500°C; (b) 50.90% V-OH/VB copolymer degraded to 500°C.

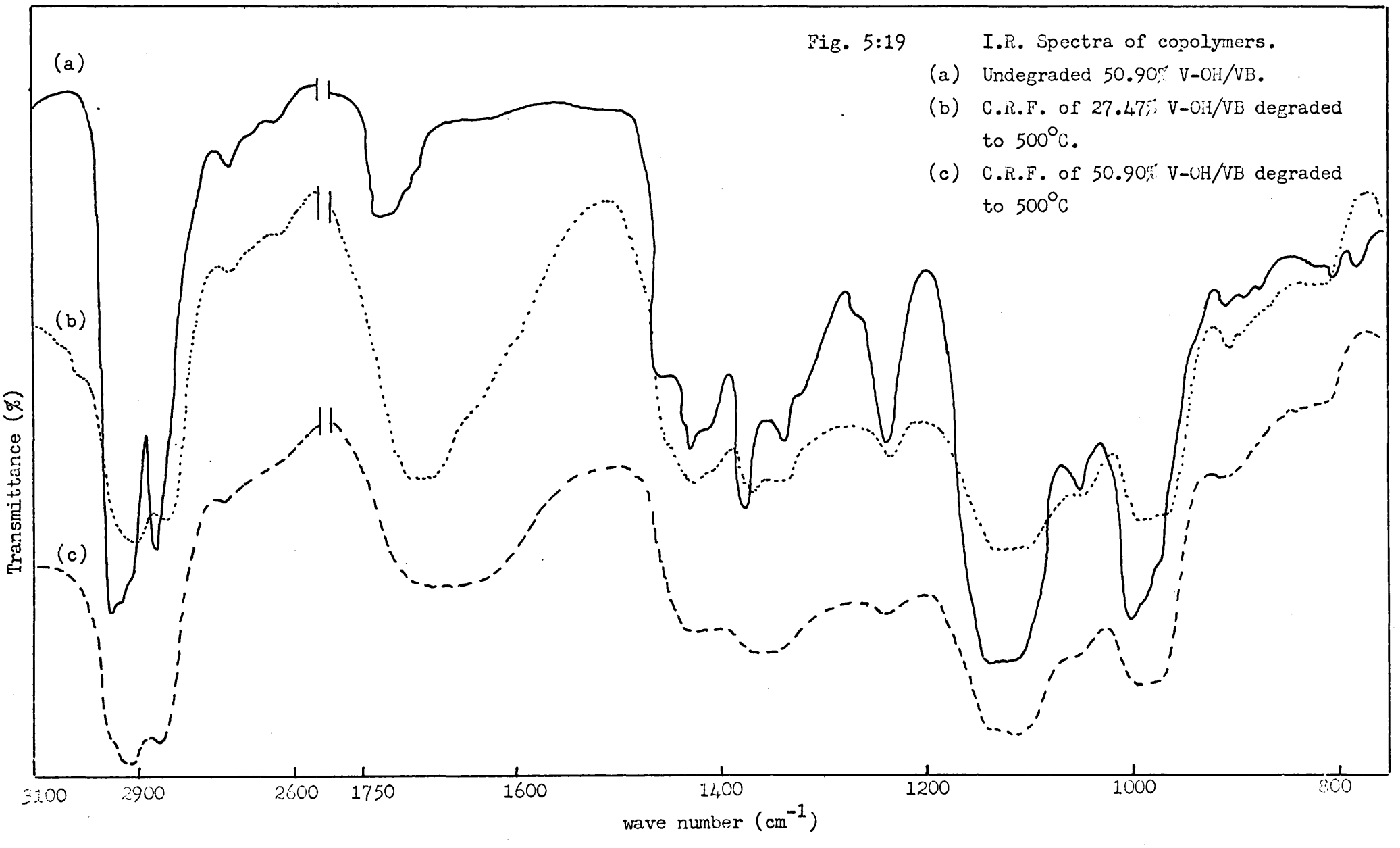


Fig. 5:19 I.R. Spectra of copolymers.

(a) Undegraded 50.90% V-OH/VB.

(b) C.R.F. of 27.47% V-OH/VB degraded to 500°C.

(c) C.R.F. of 50.90% V-OH/VB degraded to 500°C

The spectra of the C.R.F.'s are almost identical to that of the parent undegraded copolymers accept for the appearance of a few new absorptions. The peak, a little above 3000cm^{-1} (absent in the spectrum of 50·9% copolymer) and the band in the region 800 - 900 cm^{-1} arise from conjugation in the degraded copolymers. Thus i.r. of the C.R.F. proves to be a partially decomposed copolymer of low butyral and acetate contents. The carbonyl absorption of the acetate and butyral groups has shifted to lower frequency.

There was not sufficient residue for i.r. investigation.

E. Structural Changes During Degradation.

In order to investigate the structural changes which occur during the degradation of copolymers so that taken in conjunction with the formation of volatile products discussed above, conclusion might be drawn about the reaction mechanism, 50 mg samples of the copolymers were degraded in steps by programmed heating. The changes which occurred in all the copolymers were qualitatively similar so that a description of 31·66% V-OH/VB copolymer only is given in this section.

Fig. 5:20 (a), (b) and (c) shows i.r. spectra of the undegraded copolymer, the residue of the copolymer heated to first peak and C.R.F. of the copolymer heated to 500°C. I.R. spectra of n-butyraldehyde (gas phase), degradation products of the copolymer heated to first peak and second peak are shown in Fig. 5:21 (a), (b) and (c) respectively. No C.R.F. was obtained when the copolymer was heated to first peak. The i.r. spectrum of the residue in Fig. 5:20 (b) differs from that of the undegraded polymer in a slight shift in the carbonyl absorption from 1740 cm^{-1} to 1710 cm^{-1}, the absence of two peak in the 1200 cm^{-1} and 940 cm^{-1} regions and the appearance of two peaks in the region

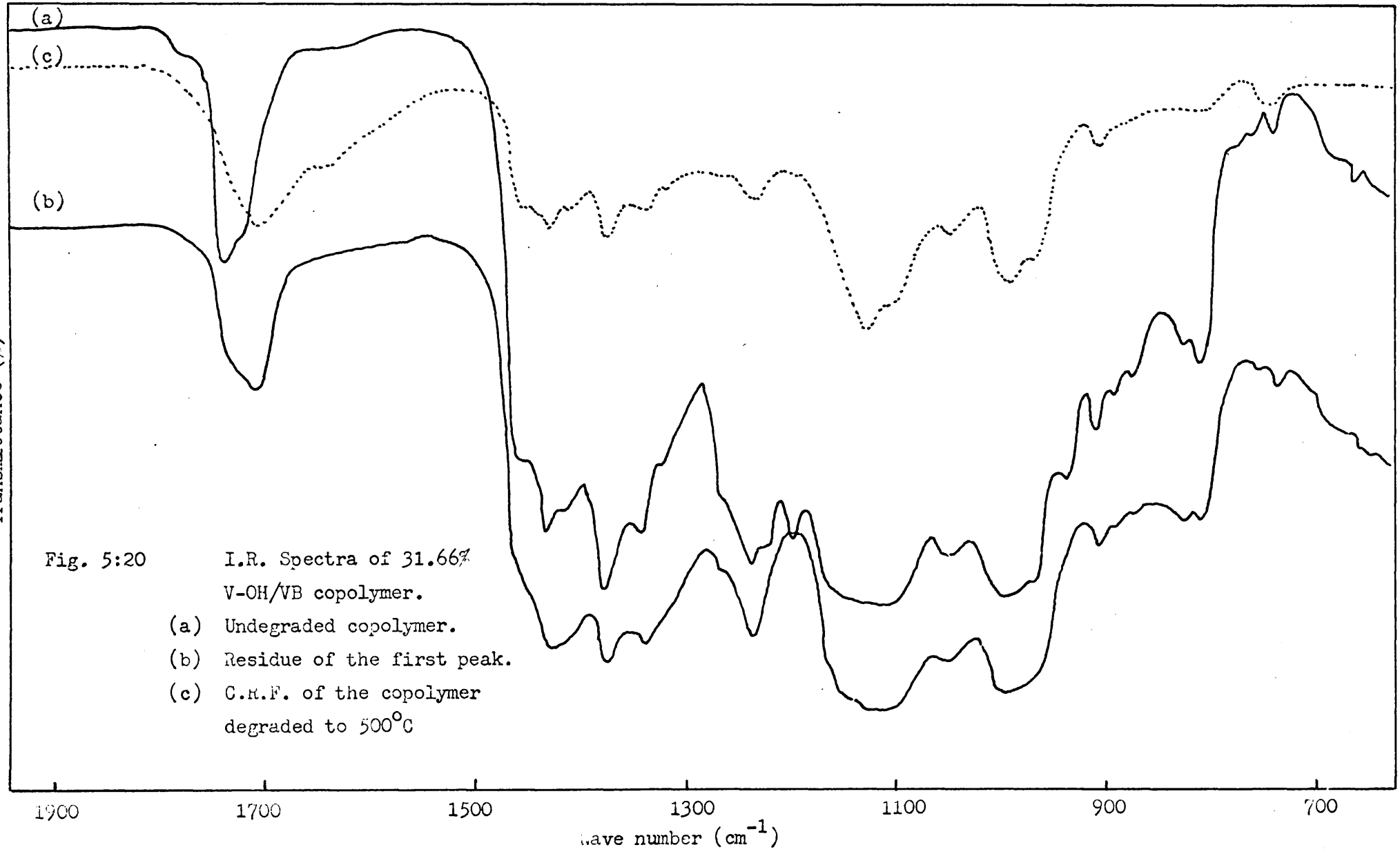


Fig. 5:20 I.R. Spectra of 31.66% V-OH/VB copolymer.

(a) Undegraded copolymer.

(b) Residue of the first peak.

(c) C.R.F. of the copolymer degraded to 500°C

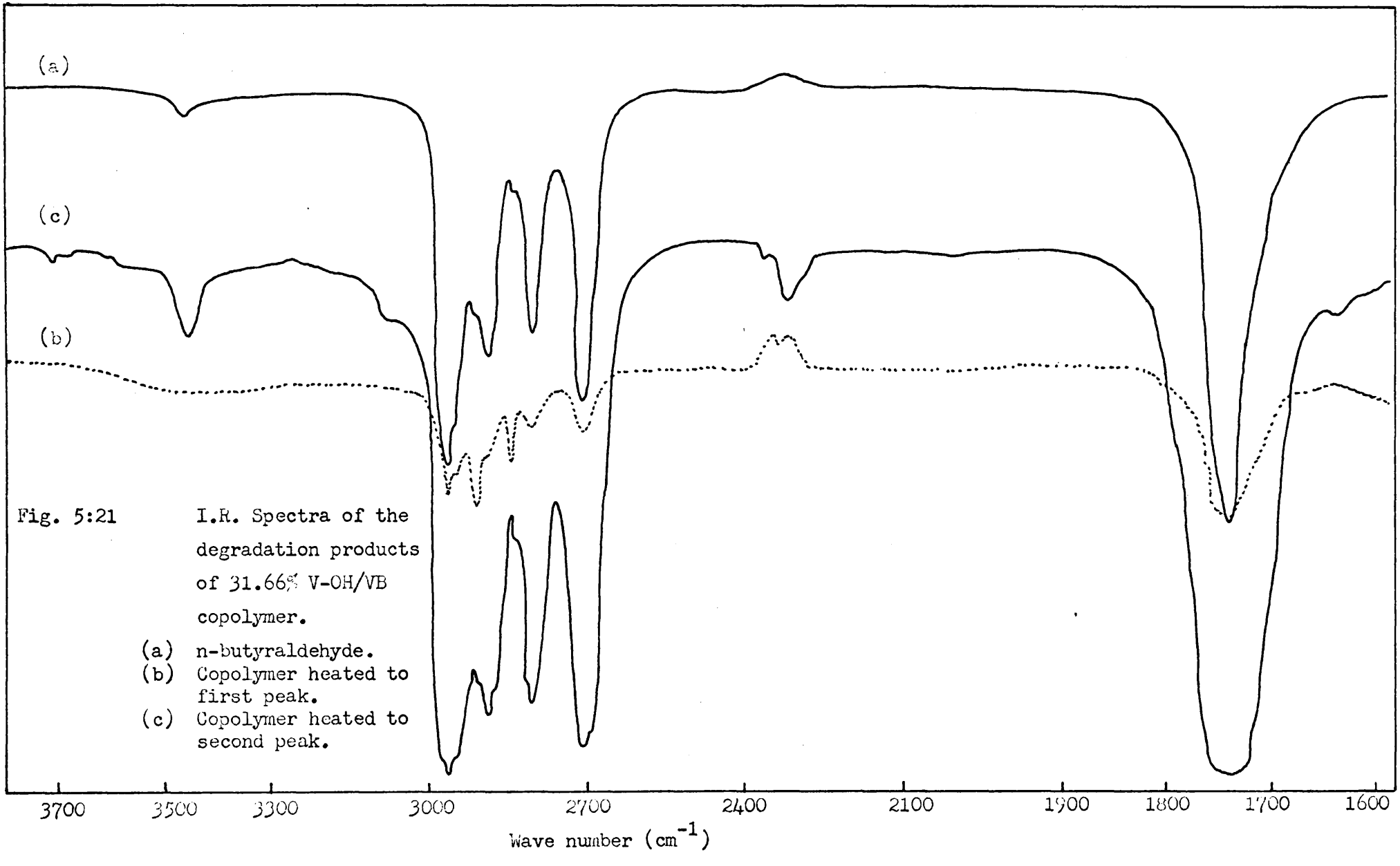


Fig. 5:21 I.R. Spectra of the degradation products of 31.66% V-OH/VB copolymer.

(a) n-butyraldehyde.
(b) Copolymer heated to first peak.
(c) Copolymer heated to second peak.

800 - 900 cm^{-1} which are associated with conjugation resulting from the elimination of acetic acid.

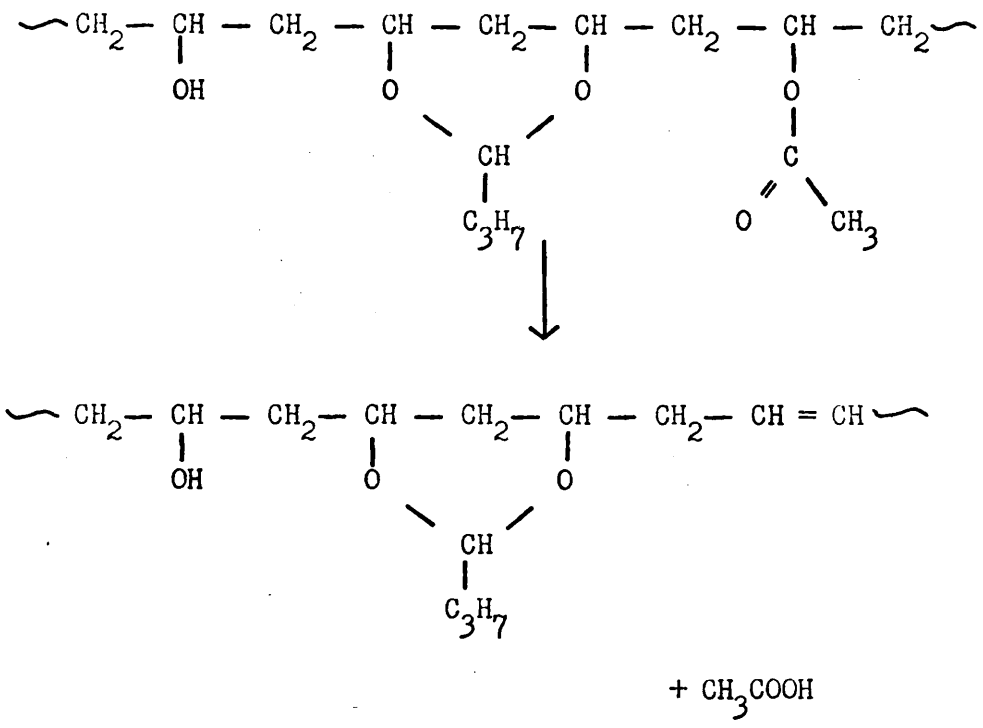


Fig. 5:21 (b) shows the degradation products of the copolymer degraded to the first peak and is accounted for in terms of acetic acid (1740 cm^{-1}) water around (3490 - 3500 cm^{-1}). Ketene and carbon dioxide were not observed at this stage probably due to the low degradation temperature. The C.R.F. of the copolymer degraded to 500°C (Fig. 5:20 (c)) shows similar absorptions. Both residue and C.R.F. show residual V-OAc and VB units in the copolymer. Investigations of the degradation products of the copolymer degraded to the second peak (Fig. 5:21 (c)) reveal that butyraldehyde and water are the main degradation products.

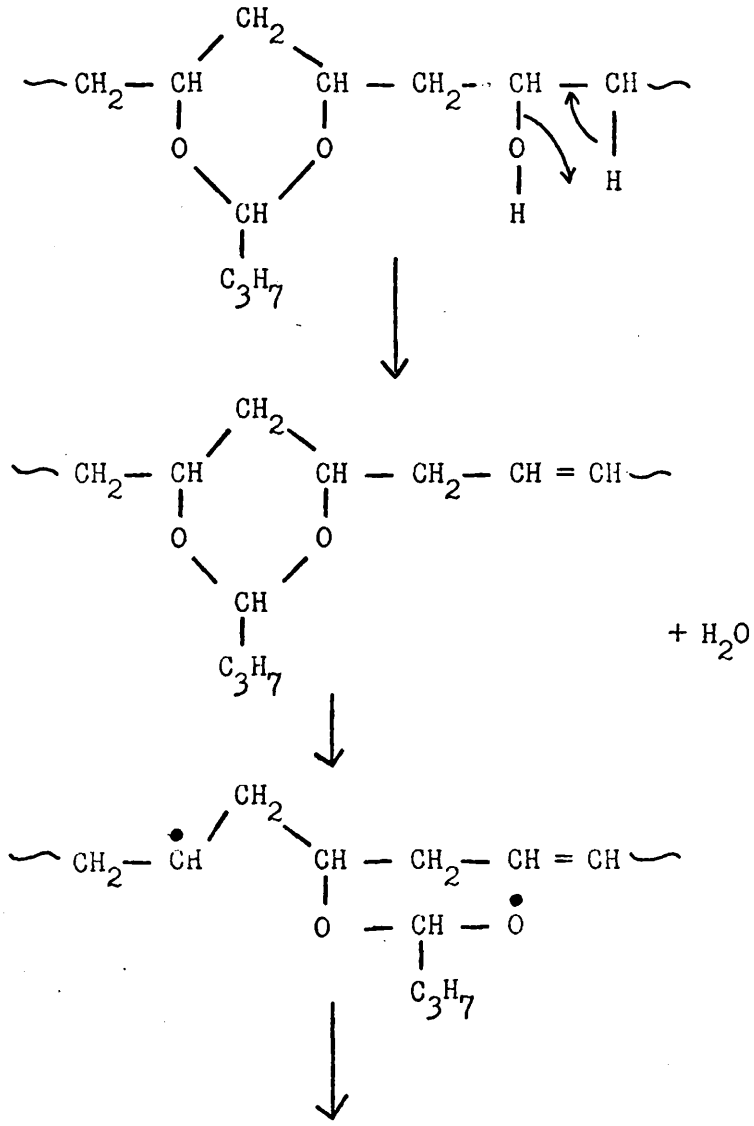
F. Proposed Reaction Mechanism.

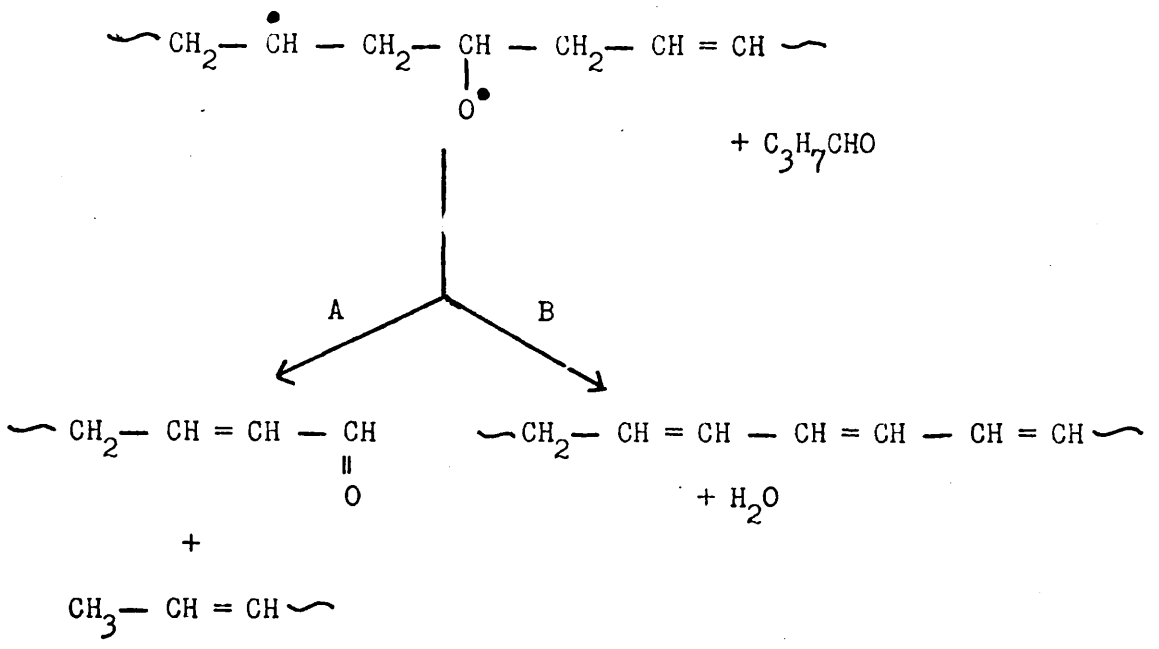
I.R. investigations of the degradation products of the copolymers of V-OH and VB degraded in steps under vacuum have shown that acetic acid and water on the one hand and butyraldehyde on the other are produced in separate steps during degradation suggesting no interaction

between two different groups in the copolymer.

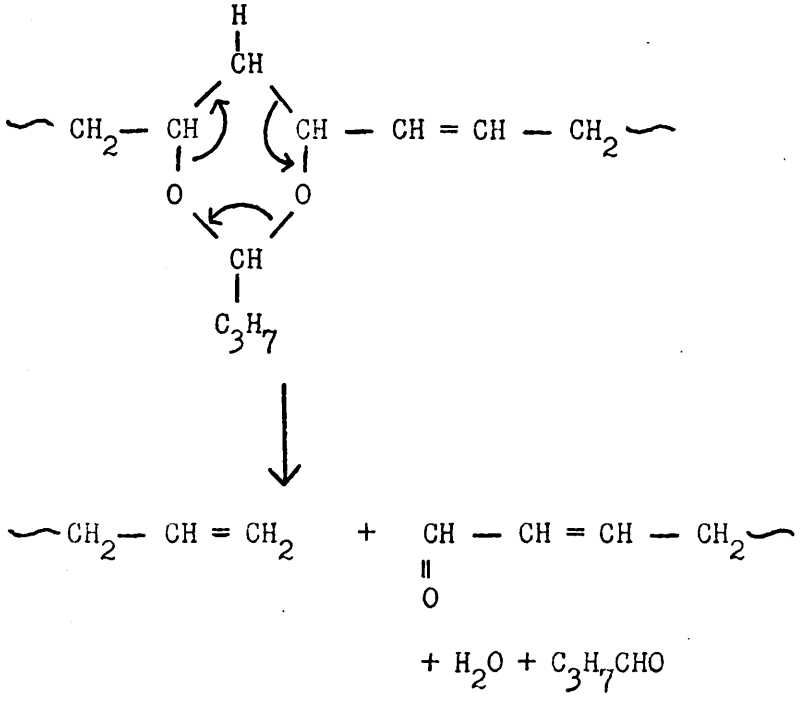
Isothermal studies under nitrogen have shown that stability to weight loss of the copolymers depends upon the concentration of butyral groups in the chain which may be associated with their electrostatic interaction and their power to block elimination of water.

The following reaction mechanism is suggested to account for the major degradation products evolved from the decomposition of the copolymers degraded in steps under vacuum.





As an alternative to the above radical process for the decomposition of the butyral units, the following molecular mechanism also leads directly to the products of reaction A above.



The very small amount of residue left and the evolution of unsaturated hydrocarbons including ethylene, propylene and isobutene suggests that the above chain scission process, whether radical or molecular plays a very large part in the reaction.

Summary.

(i) On thermal degradation PV-OH loses water in a chain reaction similar to that in which PV-OAc eliminates acetic acid and leaves a residue containing conjugated double bonds.

(ii) The formation of ketene and carbon dioxide during the degradation of PV-OH results from decomposition of acetic acid formed from the small proportion of residual acetate units in the polymer. Water is formed by elimination from the alcohol units and acetaldehyde by depolymerisation. The breakdown of polyene sequences at higher temperatures results in the formation of unsaturated hydrocarbons.

(iii) PV-OH containing some residual V-OAc units (11 - 13%) is more thermally stable than fully hydrolysed PV-OH.

(iv) The higher T_m value of PV-OH (B) than PV-OH (A) reflects the higher crystallinity of the former polymer.

(v) During the thermal degradation of PV-OH (B) the decomposition of V-OH and residual V-OAc units proceeds separately, the latter occurs at somewhat higher temperature than the former.

(vi) There is no interaction between V-OAc, V-OH and VB units during the degradation of V-OH/VB copolymer. The deacetylation of V-OAc units occurs at lower temperature than decomposition of the other two units in the chain.

(vii) The thermal stability of V-OH/VB copolymers to weight loss may depend upon the extent of electrostatic interaction between VB units in the chain. The greater interaction between them facilitates water elimination during heating resulting in less stable copolymer.

CHAPTER SIX

GENERAL CONCLUSIONS

1. Block copolymers of V-OAc and V-OH can be prepared by saponification and alcoholysis of PV-OAc, the latter being a good method for the production of PV-OH. Reacetylation of PV-OH leads to the formation of random copolymers.

2. The problems of purification and recovery of PV-OAc alcoholysed or saponified to less than 60% can be overcome using the Dialysis technique.

3. The study of hydrolysis reactions in PV-OAc has shown that the rate of the reaction depends upon solvent composition, reaction medium, reaction temperature and the nature of catalyst.

4. TGA and TVA investigations of copolymers of V-OAc and V-OH have shown that they are thermally more stable than PV-OAc.

5. Melting point data of V-OAc/V-OH copolymers have indicated that saponified copolymers are higher melting than alcoholysed copolymers reflecting higher crystallinity of the former.

6. Fully hydrolysed PV-OH is less thermally stable than PV-OH containing some residual V-OAc (11-13%) units.

7. TVA and TGA observations have shown that the stability to weight loss of V-OH/VB copolymers decreases with increase of VB units content. There is no interaction between V-OAc, V-OH and VB units during thermal degradation of copolymers of V-OH.

SUGGESTIONS FOR FUTURE WORK

Molecular weight determinations of base catalysed saponified and alcoholysed copolymers were not made in the present work. Such measurements during the course of saponification or alcoholysis would allow an assessment of the degree of cross-linking of partially hydrolysed PV-OAc and its effect on degradation properties.

It would be of great interest to compare the thermal degradation behaviour of copolymers prepared by reacetylation of PV-OH with those obtained by saponification and alcoholysis of PV-OAc.

The main chain of PV-OH consists predominantly of 1,3 - glycol repeat units [93]. Numerous investigations [13,14,94-96] concerning the structural irregularities along the chain, such as 1,2 - glycol groups, long chain and short chain non hydrolysable branches have been made using viscometric, titrimetric, i.r. and 220-MH$_z$ ^{1}H-NMR techniques. Similar investigations are necessary on the copolymers of V-OAc and V-OH from different origins.

The thermal stability to weight loss of V-OH/VB copolymers may depend upon the extent of steric interaction between VB units in the chain and the degradation temperature. Further investigation is required to confirm this theory.

REFERENCES

1. K.J. Saunders; Organic Polymer Chemistry, Chapter 1 (section 1.6.3).
2. Consortium für Electrochemische Industrie G.m.b.H; Ger. Pat; 450, 286 (1924).
3. Consortium für Electrochemische Industrie G.m.b.H; Canad. Pat; 265, 172 (1926).
4. Chemische Forschungsgesellschaft m.b.H; Ger. Pat; 642, 531 (1932).
5. F. Kainer, Polyvinyl Alkohole, Ferdinand Enke Verlag, Stuttgart, 1949, pp. 6-18.
6. Consortium für Electrochemische Industrie G.m.b.H; Ger. Pat; 685, 048 (1931).
7. F. Kainer, Melliand Textilber; 37, 559 (1956).
8. E. Hackel in Properties and applications of Poly(vinyl alcohol) (Ed. C.A. Finch), Monograph No.30, Society of Chemical Industry, London, 1968, p.1.
9. Documents from Hoechst Archives, 24, p.57.
10. P.J. Flory and F.S. Lentner, J. Polymer Sci; 3, 880 (1948).
11. P.J. Flory and F.S. Lentner, J. Polymer Sci; 5, 267 (1950).
12. I. Sakurada and G. Takahashi, Bull. Res. Inst. Chem. Fibres, Kyoto Univ; 14, 37 (1957). [C.A; 52, 13311 (1958)].
13. H.E. Harris and J.G. Pritchard, J. Polymer Sci; A2, 3673 (1964).
14. S. Imoto, J. Ukida and T. Kominami, Kobunshi Kagaku, 14, 214 (1957) [C.A; 53, 1669 (1959)].
15. Nagai, E., and N. Sagane, Kobunshi Kagaku, 12, 195 (1955).
16. Sakaguchi, Y; in Poly(vinyl alcohol), I. Sakurada, Ed; Society of High Polymer Sci; Japan, 1955 p.43.
17. R.K. Tubbs, J. Polymer Sci; Part A-1, Vol.4, pp.623-629 (1966).
18. G.O. Morrison, F.W. Skirrow and K.G. Blaikie, U.S. 2, 036, 092 (Can. Electro Prod.), c.f. U.S. 2, 116, 635; U.S. 2, 168, 827; U.S. 2, 168, 859; and U.S. 2, 179, 051.

19. W. Starck and H. Freudenberg, U.S. 2, 158, 311; T.G. McNally, C.R. Fordyce and R.H. Talbot, U.S. 2, 326, 048 (Eastman).

20. Ger. 507, 962 (Wacker); H. Hopff, U.S. 1, 955, 068 (I.G.); E. Kuehn and H. Hopff, U.S. 2, 044, 730 (I.G.); PB 40, 828; PB 40, 822; PBL 35, 512 (I.G.).

21. G.S. Stamatoff, U.S. 2, 400, 957 (du Pont).

22. Fr. 848, 460 (Nobel); Resines Polyvinylique, booklet, Societé Nobel Francaise; Rev. gén. Caoutchouc, 18, 198 (1941).

23. W.H. Mueller, Can. Chem. Process Inds; 29, 395 (1945).

24. S.N. Ushakov, Poly(vinyl alcohol) and its Derivatives [in Russian] 1 zd. AN SSSR, 1, (1960). p.413.

25. K. Noma, Chem. High Polymers (Japan), 5, 190 (1948).

26. H. Sobue, E. Soejima, and E. Yamashita, Textile Cellulose Ind. (Japan), 5, 162 (1949).

27. N. Grassie, Trans. Faraday Soc; 48, 379 (1952).

28. S.L. Madorsky, "Thermal Degradation of Organic Polymers," Interscience, New York, (1964).

29. J. Pavlinec and N.J. Kaloforov, Europ. Polym. J; 7, 1445 (1971).

30. D.L. Gardner and I.C. McNeill, J. Thermal Analysis, 1, 389 (1969).

31. H. Zimmermann, Faserforsch, U. Textil tech; 17, 228 (1966).

32. A. Servotte and V. Desreux, J. Polymer Sci; Part C, 22, 367 (1968).

33. J. Ukida, S. Usami and T. Kominami, Chem. High Polymers (Japan), 11, 300 (1954).

34. H. Futama, H. Tanaka and J. Tinnani, Kobunshi Kagaku, 14, 528 (1957).

35. H. Futama and H. Tanaka, J. Phys. Soc. Japan, 12, 433 (1957).

36. T. Yamaguchi and M. Amagasa, Kobunshi Kagaku, 18, 645 (1961).

37. T. Yamaguchi and M. Amagasa, Kobunshi Kagaku, 18, 653 (1961).

38. B. Kaesche-Krischer and H.J. Heinrich, Z. Physik. Chem. (Frankfurt), 32, 292 (1960).

39. K. Ettre and P.F. Varadi, Anal. Chem., 35, 69 (1963).

40. J.B. Gilbert and J.J. Kipling, Fuel, 41, 249 (1962).

41. B. Kaesche-Krischer, Z. Physik. Chem. (Frankfurt), 37, 944 (1955).

42. Y. Trudelle and J. Neel, Bull. Chem. Soc; France, 1969, 223.

43. Y. Tsuchiya and K. Sumi, J. Polymer Sci; A-1, 7, 3151 (1969).

44. K. Noma and K. Taniguchi, Chem. High Polymers (Japan), 9, 13 (1952).

45. A. Ya. Gelfman, D.S. Bidnaya, L. Va. Sigalova, M.G. Buravleva and V.S. Koba, Dokl. Akad. Nauk SSSR, 154, 894 (1964).

46. V.M. Kopylov, M.E. Rozenberg, S. Ya. Frenkel, S.S. Mnatsakanov, A. Ya. Sorokin and L.L. Yezhenkova,

47. H.C. Beachell, P. Fotis, and J. Hucks. J. Polymer Sci; 7, 353 (1951).

48. E.I. Kirillova, E.N. Matveeva, and A.A. Vansheidt, Plasticheskie massy, No. 2, 4 (1959).

49. G.S. Popova and Ye. V. Shuvalova, Izv. Akad. Nauk SSSR, Ser. fiz; 23, no. 10, 1205 (1959).

50. Z. Jeolinski and Z. Hippe, Roczniki Chem. 40, 257 (1966).

51. T.V. Kreitzer, Dissertation, (1967).

52. T.V. Kreitzer, Zh. prikl. spektroskopy 7, 213 (1967).

53. E.I. Kirillova, Ye. N. Matveyeva, T.G. Potapenko, F. Yu. Rachinskii and N.M. Slovachevskii, Plast. massy, No. 5, 15 (1961).

54. D. Braun and G. Vorendohre, Farbe u. Lack 69, 820 (1963).

55. F. Sadowski and E. Kuhn, Farbe u. Lack 69, 267 (1963).

56. O.I. Mayer, Farbe u. Lack 68, 853 (1962).

57. O.M. Klimova, N.I. Duvakina, L.V. Kuzmina, O.S. Romanova and A.S. Golenishcheva, Zhpkh, no. 4, 902-904 (1967).

58. V.I. Grachev, I.B. Klimenko, L.V. Smirnov and A.F. Gladkikh, Polymer Sci; USSR, 16, 367 (1974).

59. K. Noro, Methods of hydrolysis and their characteristics in Poly(vinyl alcohol) (Ed. C.A. Finch), pp.(92-93).

60. A. Skrabal, ibid; 185 A, 390 (1939).

61. N. Grassie, "Cleavage Reactions - Thermal Degradation" in "Chemical Reactions of Polymers," E.M. Fettes (Ed.), Interscience, New York, 1964.

62. I.C. McNeill, J. Polymer Sci; A 4, 2479 (1966).

63. I.C. McNeill, Europ. Polym. J; Vol. 3 p.409 (1967).

64. I.C. NcNeill, Europ. Polym. J; 6, 373 (1970).

65. I.C. McNeill, "Thermal Analysis," 417, R.F. Schwenker and P.D. Garn (Eds.), Academic Press, New York (1969).

66. I.C. McNeill and D. Neill, Thermal Analysis, 353; R.F. Schwenker and P.D. Garn (Eds.), Academic Press, New York (1969).

67. L.M. Minsk, W.J. Priest and W.O. Kenyon, J. Am. Chem. Soc; 63, 2715 (1941).

68. J.R. Roberts and M.C. Caserio, Chimie Organique Moderne, Paris, Ediscience, (1968).

69. S. Lee and I.Z. Sakurada, Physik. Chem. A 184, 268 (1939).

70. S. Sakaguchi, "The mechanism of hydrolysis of PV-OAc," in Poly(vinyl Alcohol) (Ed. I. Sakurada), The Society of Polymer Science, Tokyo, pp.43-45 (1956).

71. I. Sakurada, K. Ohashi and S. Morikawa, Kogyo Kagaku Zasshi, 45, 1287 (1942). [C.A., 44, 8161 b (1950)].

72. I. Sakurada, Gohsei Semi Kenkyn, 1-1, 192 (1942). [C.A; 44, 8161 b (1950)].

73. I. Sakurada, Kogyo Kagaku Zasshi, 45, 1290 (1942).

74. Sakurada and his co-workers, Velocity of the hydrolysis reaction, in Poly(vinyl alcohol) (Ed. C.A. Finch), pp.90-101.

75. Z. Patel and H. Watson, J. Indian Inst. of Science, 16, A, 55 (1933).

76. E. g., A. Skrabal and E. Singer, Monatsh; 40, 363 (1919); 41, 339 (1920).

77. A. Katchalsky, N. Shavit and H. Eisenberg, J. Polymer Sci; 13, 69 (1954).

78. F. Arranz and M. Ashraf Tahir, Rev. de - Plasticos Modernos, 160, Oct; (1969).

79. E.W. Eckey, 'Ester interchange,' in Encyclopedia of Chemical Technology (Eds. R.E. Kirk and D.F. Othmer), Interscience, New York, 5, pp.817-823 (1950).

80. A.J. Mee, Physical Chemistry p.324. 6 ed.

81. J. Polymer Sci; 39, pp.70-73 (1959).

82. J.B. Gilbert and J.J. Kipling, Fuel, 42, 5 (1963).

83. R.C. Seymour and A.R. Westwood, Europ. Polymer J; 7, 419 (1971).

84. A. Jamieson, Ph.D. Thesis, University of Glasgow, 1972.

85. J.C. Daniel and J.M. Michel, J. Gas Chromat., 5, 437 (1967).

86. D.L. Gardner, Ph.D. Thesis, University of Glasgow, (1969).

87. N. Grassie and R. McGuchan, Research Report, University of Glasgow, (1971).

88. M.A.J. Mohammad, Ph.D. Thesis, University of Glasgow, (1970).

89. B. Kaesche - Krischer and H.J. Heinreich, Chemic. Ing. Techn; 32, 598 (1960).

90. A. Kayast, T. Nakomo and T. Motoyama, Kobunshi Kagaku 20, 217, (1963).

91. C.H. Bamford and M.J.S. Dewar, J. Chem. Soc; 2877 (1949).

92. A. Scotney, Ph.D. Thesis, University of Hull, (1967).

93. C.S. Marvel and C.E. Denoon, Jr., J. Amer. Chem. Soc., 60, 1045 (1938).

94. K. Imai and U. Maeda, Kobunshi Kagaku, 16, 176 (1959).

95. E. Nagai and N. Sagane, Kogyo Kagaku Zasshi, 59, 794 (1956).

96. K. Fujii, J. Polym. Sci., D, 5, 431-540, particularly 527-531 (1971).